

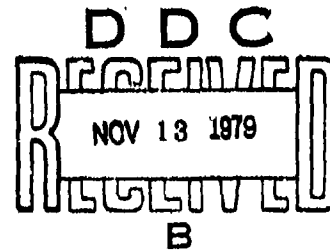
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AFML-TR-79-4041

HIGH SOLIDS COATING SYSTEM

DeSoto, Incorporated
Research and Development Center
1700 S. Mt. Prospect Road
Des Plaines, Illinois 60018



April 1979

TECHNICAL REPORT AFML-TR-79-4041

Final Report for Period August 1977 to January 1979

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This technical report has been reviewed and is approved for publication.

Daniel E. Prince
DANIEL E. PRINCE, Project Engineer
Coatings & Thermal Protection
Materials Branch
Nonmetallic Materials Division

William L. Lehn
WILLIAM L. LEHN, Technical Manager
Coatings & Thermal Protection
Materials Branch
Nonmetallic Materials Division

FOR THE COMMANDER

J. M. Kelble
J. M. KELBLE, Chief
Nonmetallic Materials Division

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The goal of this program is the development of a 65% volume solids, sprayable (airless electrostatic method), polyurethane exterior aircraft coating meeting MIL-C-83286 performance specifications. A high solids coating can significantly reduce solvent emissions and help the Air Force meet EPA/OSHA requirements for reduced environmental pollution and increased worker safety.		

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20. One formulation consisting of a combination of Acryloid AU-568 (oxazolidine), NIAx PCP-0300 (polyol), and Desmodur N-100 (polyisocyanate) exhibited performance properties close to MIL-C-83286. Additional effort is required to simultaneously maximize coating flexibility and solvent (aircraft fluid) resistance. The pot life of the mixed two-package system and the final spray viscosity also must be improved.

Potential polyol and polyisocyanate candidates can be successfully screened using concentration-viscosity diagrams. The effects of solvent on solution rheology were greater than expected.

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FOREWORD

This final report covers the period August 15, 1977 to January 15, 1979 under Contract F33615-77-C-5101 for the Air Force Materials Laboratory, Air Force Wright Aeronautical Laboratories (AFSC), Wright-Patterson AFB, Ohio. The Contract was initiated under Project Number 2422, "Protective Coatings and Materials", Task Number 242201, "Protective Coatings and Materials." The project engineers were Mr. Michael J. Moscyński from August 1977 to February 1978 and Mr. Daniel E. Prince from March 1978 to January 1979.

Funding for determining the applicability of the high solids polyurethane coatings to steel substrates for potential use in the automotive or appliance industry was supplied by Mr. Charles Darvin, Industrial Environmental Research Laboratory, Environmental Protection Agency, Cincinnati, Ohio.

This report was prepared by DeSoto, Incorporated, Research and Development Center, Des Plaines, Illinois. The work was performed under the direction of Dr. Richard E. Wolf. This report was released by the author in February 1979.

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I. Introduction and Summary

In recent years, the effect of the varied industrial effluents and waste materials which find their way into the environment has come under scrutiny. For the coatings industry and coatings users, the main concern is the solvent emission from the application of paints. Historically, the first environmental constraints were applied to the type of solvents emitted into the atmosphere in an effort to reduce the photochemical smog production (Rule 66, Los Angeles County). These regulations were designed to control the amount of photochemically reactive solvents in relationship to the other, acceptable solvents. The total amount of solvent emission was not controlled. More recently, however, economic parameters, coupled with the energy crisis and an increased awareness of impacts on the environment, has lead to pressures to reduce the total amount of solvent emission. The main choices available to the coatings industry are water-based systems, ultraviolet light curable systems, and/or high solids systems. One of the more attractive approaches for the aerospace industry is high solids coating systems.

High solids coating systems offer a number of attractive properties regarding both economic and environmental concerns. High solids coatings can eliminate the use of photochemically reactive solvents as well as drastically reduce the total solvent emissions necessary to deliver equivalent quantities

of paint products. This reduction in total solvent and increased paint solids can result in economic gains through decreased freight, handling, and storage costs. Production rates can be increased, and fire hazards can be reduced. The materials used in high solids systems should be similar to currently used materials so that only minor changes in production and application equipment can be expected.

This program, supported by the Air Force Materials Laboratory, Wright-Patterson Air Force Base, under contract F33615-77-C-5101, is part of a continuing effort toward the development of a high performance, 65% volume solids, two-package polyurethane exterior coating for military aircraft, suitable for application by airless electrostatic spray.

A comparison of the performance properties required for military aircraft to those of Fruehauf Engineering may be found in Table 1. The performance specifications for Fruehauf Engineering, a manufacturer of trucks and truck parts, are considered to be representative of the transportation industry.

As a final result, one formulation, a combination of Acryloid AU-568, (oxazolidine), NIAX PCP-0300, (polyol), and Desmodur N-100, (polyisocyanate) (2408-9), was found to exhibit performance properties which closely approximate

TABLE 1

Comparison of Typical Performance Specifications

WIL-C-62236		FRUEHAUF ENGINEERING	
5% Salt Spray	No blistering, cracking, corrosion, or loss of adhesion after 500 hours of exposure.	No blistering, cracking, corrosion, or loss of adhesion after 500 hours of exposure.	
100% relative humidity	No blistering, cracking, softening, or loss of adhesion after 720 hours of exposure.	Not applicable.	
Accelerated weathering	After 500 hour exposure the coating should exhibit 60% impact flexibility, no more than 10% loss of original gloss, and no color change.	No color change, chalking, checking, or other film defects after 250 hours of exposure.	
Fluid Resistance	A decrease of no more than one pencil hardness unit after immersion in water (4 days, 100°F), lubricating oil (24 hours, 250°F), hydrocarbon fluid (7 days, room temperature), and hydraulic fluid (7 days, room temperature). A decrease of no more than two pencil hardness units after immersion in Skydrol 500B fluid (7 days, room temperature).	No cracking, blistering, or checking after 100 hours in distilled water at 100°F.	
Film Flexibility	No cracking, crazing, or loss of adhesion of coating when elongated 60% by impacting mandrel.	No cracking or loss of adhesion when deformed 180° over conical mandrel (maximum elongation - 26%).	
Low Temperature Flexibility	No cracking or loss of adhesion when bent around 3/8 in (9.5 mm) diameter cylindrical mandrel after four hours at -65°F (-54°C). (Test immediately after removal from cold box).	Not applicable.	
High Temperature Resistance	No loss of adhesion or flexibility after four hours at 300°F (149°C).	Not applicable.	
Reverse Impact	Not applicable.	>80 in-lbs.	
60° Gloss	>90	>90	

the program goals.

The first phase of this program was directed toward the analysis of viscosity-concentration profiles and the effect of high shear rates on the viscosities of polymer/solvent combinations. From the data obtained, methyl ethyl ketone (MEK) was found to be the solvent of choice in these high solids coatings because of its effectiveness in lowering the viscosities of the polymer solutions.

As measured with high shear instrumentation, the viscosities of these high volume solids oligomer solutions exhibit a reversal in their rheological properties relative to the viscosities obtained at low shear rates and low volume solids. Although the possibility exists that a certain degree of this reversal may be due to an artifact of the instrumentation, a trend toward pseudoplasticity at high shear for these high volume solids oligomer is clear.

The formulator of high volume solids coatings should be cautious in choosing a given system based simply on low shear viscosity measurements. If the present data is indicative of the true behavior of these solutions, the rheological characteristics of high solids systems may lie on a serpentine viscosity-concentration profile display, and the specific behavior for a desired application must be considered before a system selection is made.

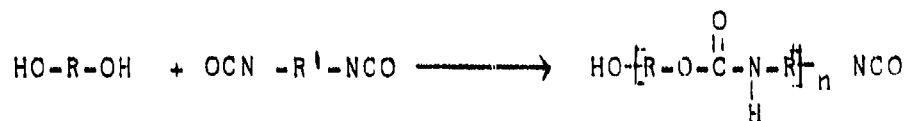
The second phase involved the evaluation of clear films. The unpigmented polyols, formulated with isocyanate crosslinking agents, were qualitatively assessed to obtain their spray properties and tested for final film properties.

Three polyols, Acryloid AU-568, an oxazolidine from (Rohm and Haas Company), Cargill 5760 (Cargill, Inc., Chemical Products Division), and NIAx PCP-0300 (Union Carbide) were selected for continued evaluation and formulation optimization.

The three polyols identified in the second phase for optimization were pigmented with titanium dioxide, cured with Desmodur N-100 (Mobay Chemicals), and evaluated for physical and chemical properties during the third phase. Good fluid resistance properties were maintained when these systems were pigmented, but the low temperature flexibility performances were degraded.

The final phase of the program consisted of blending the various components previously evaluated to achieve a formulation which closely approximates the program goals as specified in MIL-C-83286 and in Appendix B.

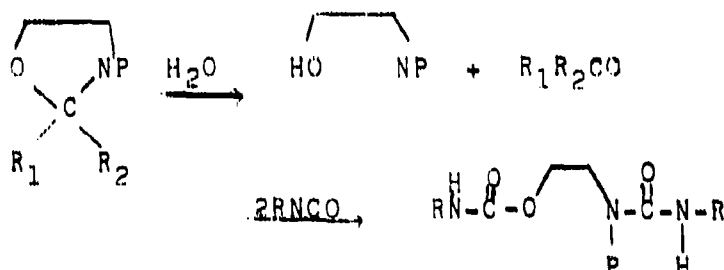
The theory behind polyurethane chemistry is not complex. Hydroxy terminated prepolymers (polyols) are reacted with isocyanate terminated prepolymers (polyisocyanates) to form a polyurethane.



The polyol and polyisocyanate may be formulated into a two-component coating formulation. One limitation of this type

of system is the short pot life (particularly when the usually necessary catalyst is used).

An additional approach to two-component coatings system is based on blends of a polyfunctional oxazolidine with isocyanate. Properly chosen oxazolidines are weak bases, have no active hydrogen, and are very rapidly converted to the parent alkanolamine which reacts with a polyisocyanate to form an excellent coating. The chemistry of the oxazolidine ring is such that it may be conveniently introduced into a variety of polyfunctional and polymeric matrices.



P = Polymeric Substrate

Acryloid AU-568, an oxazolidine from Rohm and Haas Company (originally supplied as experimental resin QR-568), was evaluated for incorporation into high solids coating systems. Because the reaction of the oxazolidine with water forms the alkanolamine, the Acryloid AU-568 was screened with the polyols also being evaluated.

An investigation of the feasibility of transferring high solids coatings technology developed under this con-

tract to the needs of the transportation and appliance industries was performed. The funding for the feasibility study was provided by the Environmental Protection Agency via the AFML(WPAFB). The executive summary of this work may be found in Appendix A.

II. Experimental

A. Viscosity-Concentration Profiles

1. Polyol Screening

The viscosity-concentration profiles were constructed from data obtained by measurements made with the equipment described in Table 2.

<u>Table 2</u>	
<u>Four Methods of Measuring Solution Viscosities</u>	
<u>Viscometer</u>	<u>Description</u>
1. #2 Zahn Cup:	Useful, unsophisticated, providing low, constant shear.
2. Brookfield Viscometer (Synchroelectric-Model RVT):	Provides nonuniform shear over 0.52 to 49.2 sec^{-1} range.
3. Wells-Brookfield Micro (Model LVT):	Plate and Cone assembly, with 1.15 to 230 sec^{-1} shear range.
4. Haake Rotovisco (Model RV-3):	Bob and Cup attachment, with 74 to 12,000 sec^{-1} shear range.

The polyols evaluated for viscosity characteristics were Acryloid AU-568 (Rohm and Haas Company), Cargill 5760 (Cargill, Incorporated, Chemical Products Division), Multron R-221-75 (Mobay), Aroplaz 6025-A1-80 (Archer, Daniels, and Midland), NIAx Polycaprolactone polyols (Union Carbide), and Pluracol series (BASF Wyandotte). The solution concentrations at which the polyols were evaluated were dependent on the polyol. The solvents used in the viscosity studies were 2-ethoxyethyl acetate, methyl ethyl ketone (MEK), methylisobutyl ketone (MIBK), n-butyl acetate, tetrahydrofuran (THF), and 1,4-dioxane.

2. Polyisocyanate Screening

The solution viscosity of Mobay Chemical Corporation's experimental polyisocyanate, L-2291, was compared to Desmodur N-100 (Mobay) polyisocyanate. A modification of Desmodur N-100, L-2291 was designed to have lower viscosity for high solids application.

The viscosities of the Desmodur N-100 solutions and the L-2291 solutions were measured with a Wells-Brookfield Micro Viscometer at 298°K (77°F). The Desmodur N-100 material was evaluated at 55, 65, 75, and 85 percent volume solids in the solvents used also for polyol evaluation.

At the 85 percent volume solids level, the viscosity reached a high value. The L-2291, following the same trend towards a high viscosity, was evaluated at only the 65 and 75 percent volume solids levels.

3. Titanium Dioxide Dispersions

Dispersions of the selected polyols and titanium dioxide were made as indicated in Table 3.

The best material in terms of maximizing the volume solids of the TiO_2 dispersion is the Acryloid AU-568. To emphasize the good performance of this pigment/polymer combination, successful grinds were made at 60 and 65 percent volume solids. The mill charge yield at the 60 percent volume solids was ~0.96, i.e., ninety-six percent of the material added to the ball mill was recovered by simply pouring it from the mill. The 65 percent volume solids has a yield of ~0.92. In contrast to this,

Table 3
Titanium Dioxide Dispersions*

Pigment Blend	Material	Weight %	Volume %
Acryloid AU-568/TiO ₂	AU-568	24.99	40.64
	TiO ₂	59.72	26.40
	Urethane Grade	15.29	32.96
	MEK		
NIAX PCP-0300/TiO ₂	NIAX PCP-0300	17.76	22.80
	TiO ₂	47.94	17.20
	Urethane Grade	34.30	60.00
	MEK		
Cargill 5760/TiO ₂	Cargill 5760	25.47	37.89
	TiO ₂	55.88	23.64
	Urethane Grade	18.65	38.47
	MEK		

* A charge of 450 ml was blended in a quart ball mill with 2000 g of 1/2 inch Burundum grinding media. The dispersion was milled 24 to 36 hours until a Hegman fineness of grind greater than 7NS was reached.

a TiO_2 /Cargill 5760 system at 60 percent volume solids has a yield of only 0.65 at a similar PVC level. The viscosities at varying shear rates were measured on the Haake Rotovisco viscometer.

B. Film Formation

1. Clear Films

The unpigmented polyols formulated with Desmodur N-75 or Desmodur N-100 were qualitatively assessed as to their spray properties (atomization at approximately 3.5 kg/cm^2 (50 lb/in^2) and flow), and tested against the final film property requirements.

The screening tests used in evaluation of the films were performed according to tests outlined in Appendix B. The tests were run on, at least, duplicate panels.

The catalyst used throughout the formulations was dibutyl tin dilaurate (DBTDL) at a level of approximately 4×10^{-4} gram/gram total resin except for the Acryloid AU-568, NIAX Caprolactone polyols and the Polymeg based formulations. Catalyst was not used with the Acryloid AU-568 because the reaction of isocyanate and the oxazolidine group in the presence of atmospheric moisture is rapid enough to give tack free films in several hours. The high reactivity of the primary hydroxyl groups of the NIAX Caprolactone polyols and the Polymeg materials at the 4×10^{-4} gram/gram total resin level of the catalyst leads to unacceptably short gel times

of approximately 600 seconds (10 minutes). Reduction of the catalyst by a factor of two results in a gel time of approximately 3.6ks (1 hour), sufficient time to obtain films for testing.

2. Pigmented Films

The polyols which demonstrated good overall performance during initial screening were pigmented with titanium dioxide, blended with Desmodur N-100, cured, and tested.

The polyols Cargill 5760 and Acryloid AU-568 were pigmented with titanium dioxide R-960.09 (E.I. duPont de Nemours & Co.). The starting point formulation was extrapolated from sample sand mill grind formulas given by Rohm and Haas Company for their high solids material Acryloid AU-568. MEK was used as the sole added solvent in these ball mill grinds. The pigment was ground in the solutions for approximately 48 hours. The Cargill 5760 based system was formulated at 43% volume solids, 70% weight solids, and a pigment to binder ratio, PBR, of 2.9 which corresponds to a 47% pigment volume concentration, PVC. For the Acryloid AU-568 based material, the pigment dispersion characteristics were 44% volume solids, 70% weight solids, a PBR of 2.9, and 44% PVC.

Upon standing, the pigment in both dispersions settles. In the Cargill 5760 system, the sediment is not compact; it can be easily penetrated with a spatula blade and redispersed with hand stirring. The sediment in the Acryloid AU-568 system

is hard; it cannot be penetrated easily with a spatula blade and it does not redisperse with hand stirring. The pigment will redisperse when agitated for approximately 1 hour on a paint shaker.

A second dispersion of TiO_2 in the Rohm and Haas Acryloid AU-568 was made at a slightly higher volume solids. The mill charge was calculated at 50% volume solids, 77% weight solids, and a PBR of 2.81 (~44% PVC). Again, MEK was used as the sole added solvent (Acryloid AU-568 is supplied at 85% weight solids in 2-ethoxyethyl acetate). The volume solids was increased in an attempt to raise the dispersion viscosity to retard settling. The dispersion still had a low viscosity (subjective, instrumental viscosities were not determined since these materials were used for film preparation) and had hard settling.

The NIAx Caprolactone polyol PCP-0300 was also pigmented using TiO_2 . The composition of the final grind formula was 65 percent weight solids, 40 percent volume solids, a pigment to binder ratio of 2.54, and a pigment volume concentration of 41 percent. The solvent used in the grind was MEK. The pebble mill was originally charged at 76% weight solids and 55% volume solids (PBR=3.7). However, the consistency of the charge was pastelike, too high in viscosity for pigment dispersion. Dilution of the charge with MEK to ~69% weight solids, 45% volume solids did not adequately reduce the viscosity (the PCP-0300 concentration at this point was ~15% weight solids).

The charge was further modified by the addition of more PCP-0300 to bring the volume solids to 50%, to a PBR of 2.54. The fineness of grind (Hegman) was greater than 7NS after approximately 24 hours of milling. The dispersion obtained was thixotropic in nature; although the grinding media could be heard tumbling when the ball mill was rotating, the dispersion did not flow freely when transferring the charge out of the mill. The pigment did settle but the sediment was soft and it would redisperse with hand stirring.

Two other grinds of TiO_2 in NIAX PCP-0300 were made. Both were formulated to 40% volume solids but differed in the proportion of pigment to binder. One grind had a PBR of 2.45 which resulted in a weight solids of 65%; the other grind had a higher level of pigment with a PBR of 5.5 and a weight solids of 70%. The dispersion attempted at PBR=5.5 gave a paste like consistency to the coarsely mixed materials. The total concentration of solids was, therefore, reduced to 60% weight solids, 30% volume solids. At this composition, the grinding media could be heard to tumble as the mill was rotated. Both grind formulations were placed on the roller mill for 30-36 hours, after which time they gave Hegman grind readings greater than 7NS. (Laboratory practice was to allow grind formulations to roll until a minimum Hegman grind reading of 7NS was reached. Practically precluded measurements beyond this value.) The TiO_2 /PCP-0300 grind at 40% volume solids was very fluid and poured freely. The TiO_2 /PCP-0300 grind wt 30% volume solids still had a paste like consistency and did not pour freely.

Settling of the pigment has been observed in the TiO_2 /PCP-0300 but the pigment rich layer is soft (easily penetrated by a spatula blade) and the pigment redispersed with hand stirring.

3. Polyisocyanate Substitution

Two isocyanate functional materials, L-2291 (Mobay Chemicals) and DDI 1410 (General Mills), were examined as curing agents and compared to coatings which used Desmodur N-100 as the curing agent.

C. Formulation Modification

In an effort to achieve a formulation which meets the program requirements, the polyol/isocyanate systems were modified by the addition of oligomeric diols or polyisocyanates.

1. Polyol Blends

The Acryloid AU-568/Desmodur N-100 system was modified by the addition of oligomeric diols. The diols used were Pluracol P-410 (a polyether diol), QO Polymeg 650 (poly(tetramethylene oxide) diol), Cargill 5760, and NIAx PCP-0200 and PCP-0300 (both poly(caprolactone) derived diols). The system, before modification, exhibits good fluid resistance but poor flexibility performance. To improve the flexibility properties, formulations were made in which ten and twenty-five weight percent of the Acryloid AU-568 was replaced with the selected polyols.

Analogous to the modification of the Acryloid AU-568/Desmodur N-100 by the addition of oligomeric diols, the NIAx

PCP-0300/Desmodur N-100 and Cargill 5760/Desmodur N-100 systems were modified. The NIAX PCP-0300/Desmodur N-100 was blended with Acryloid AU-568 and Cargill 5760. The Cargill 5760/Desmodur N-100 was blended with Acryloid AU-568 and NIAX PCP-0300.

2. Polyisocyanate Blends

In analogy to the oligomeric diol blending studies, a series of coatings was prepared in which ten or twenty-five weight percent of the polyisocyanate in the Acryloid AU-568/Desmodur N-100 and Acryloid AU-568/L-2291 systems was replaced with DDI 1410.

D. Airless Electrostatic Spray

A quart kit (final volume = 1/2 gallon) of the "best" formulation (2408-9) was prepared. The two component polyurethane topecoat formulation was blended and applied to five unprimed aluminum panels by airless electrostatic spray. (REH equipment from Randsburg Corporation and pump system from Graco). The orifices and pressures used during spraying were varied for each panel. (See Table 4)

Table 4

Airless Electrostatic Spray Variables

<u>Panel</u>	<u>Orifice #</u>	<u>Pressure (psi)</u>	<u>Comments</u>
1	13	1100	----
2	13	1380	----
3	15	1380	----
4	"large"	1380	----
5	--	1380	no charge applied during spraying

The panels were cured and evaluated for film appearance.

III. Results and Discussion

A. Viscosity - Concentration Profiles

1. Polyols

Data obtained from measurements made with a #2 Zahn cup indicate that of the solvents tested, MEK appears to be the solvent of choice for obtaining the oligomeric solutions of lowest viscosity. However, this data provides no information concerning the behavior of these solutions at higher and variable shear rates. (Fig No. 1)

When the viscosities of these oligomeric solutions are measured on a Brookfield viscometer at various shear rates, a different kind of behavior becomes apparent. At lower volume solids, these solutions appear to be dilatant. However, the higher volume solutions appear to approach Newtonian behavior in their rheological characteristics. (Fig No. 2)

In an attempt to gain insight into why methyl ethyl ketone had the greatest power to decrease the viscosity of the polymers evaluated, the Brookfield RVT viscosities were replotted following a procedure advanced by Erickson in studying the rheology of high solids systems. Erickson found that a plot of $W/\ln(\eta/\eta_s)$ versus W gave a straight line for several oligomer-reactive diluent solutions. W is the weight fraction of the oligomer, η is the viscosity of the solution at composition W , and η_s is the viscosity of the neat solvent or reaction diluent. Erickson's theory parameterized this concentration-viscosity relationship as:

$$W/\ln (\eta/\eta_s) = \frac{1}{(\eta)_w} + kW \quad (1)$$

where $(\eta)_w$ is the weight intrinsic viscosity; it is related to the normal intrinsic viscosity by

$$(\eta)_w = \rho_s (\eta) \quad (2)$$

where ρ_s is the solvent density. The slope of equation (1) is given by

$$k = \frac{1}{\ln(\eta_o/\eta_s)} - \frac{1}{(\eta)_w} \quad (3)$$

where η_o is the viscosity of the oligomer. Erickson's guidelines for the lowering of the solution viscosity of concentrated systems were the selection of solvents that made $(\eta)_w$ small (i.e., decrease solvent-polymer interactions) and the use of oligomers/polymers of low viscosity which usually means low molecular weight.

The Brookfield viscosities of various polyol-solvent combinations were plotted as directed by equation (1) to determine if the data would yield straight lines, and if information could be extracted regarding the effects of solvent quality on viscosity. The usual practice is to classify a solvent as a good solvent for a polymer if it gives a large (η) whereas a small or smaller (η) would label the solvent as poor.

Several plots of data according to equation (1) were found to be nonlinear. Figure 3 is an example of the behavior observed. The inapplicability of equation (1) to the systems under study in this work is most likely due to the

non-Newtonian nature of the solutions. For concentrated non-Newtonian polymer solutions there is evidence that good solvents (large $[\eta]$) are preferred for minimizing viscosities in contradiction to Erickson's findings for Newtonian solutions.

The non-Newtonian nature of the polymer solutions requires that the viscosities be examined at several well defined shear rates. The Brookfield Synchro-Lectric Viscometer provides only a limited shear rate range. Several of the systems examined on the Brookfield Synchro-Lectric, model RVT were re-examined using a Wells-Brookfield Micro Viscometer, model LVT. The measuring head on this plate and cone instrument is equipped with a water jacket to provide temperature control. Figures 4, 5, and 6 show the viscosities of Acryloid AU-568 and Cargill 5760 solutions obtained throughout this shear rate range as a function of concentration. As observed in previous measurements, the solutions using methyl ethyl ketone as solvent show the lowest viscosities at equivalent concentrations. It should also be noted that the viscosities were found to increase with increasing shear rate when measured on the Brookfield Synchro-Lectric (Figures 7 and 8) whereas the viscosities decrease with increasing shear rate when measured on the Wells-Brookfield.

The shear rates obtainable with the Wells-Brookfield viscometer are quite limited when compared to the high shear rates expected in spray application of coatings. The range of shear rates reported in spraying paints is 1000 sec^{-1} to $40,000 \text{ sec}^{-1}$. Therefore, measurements were also made using the

Haake Rotovisco viscometer. A decrease in viscosity with increasing shear rate was also observed on the Haake Rotovisco unit. These results are consistent with those obtained in the Wells-Brookfield.

Solution viscosity-concentration curves for many of the polyols evaluated are presented in Figures 9 through 14. Figure 15 summarizes some of the data for the Desmodur N-100 material. An Erickson type plot for the Rohm and Haas Acryloid AU-568 system at several different shear rates is given in Figure 16. Again, the curves are nonlinear in agreement with the Brookfield Viscosity data of Figure 3.

2. Polyisocyanates

From the data collected, the viscosities of the L-2291 solutions are approximately one-half the value of the Desmodur N-100 solutions at the same shear rates and concentrations. (Tables 5 and 6). The viscosities of the 75 percent volume solids solutions of the L-2291 polyisocyanate are approximately equal to the viscosities of the 65 percent volume solids Desmodur N-100 solutions. Using the criterion that a viscosity range of 40 cps to 150 cps is required for spraying, it would be expected that the L-2291 solutions at 75 percent volume solids would atomize adequately but not the 75 percent volume solids solution of Desmodur N-100.

For the 65 and 75 percent solutions of the L-2291 and Desmodur N-100, methyl ethyl ketone (MEK) is the preferred solvent for viscosity reduction. Tetrahydrofuran (THF) is

Table 5

Desmodur N-100 Solution Viscosity*

Volume Concentration	Solvent	SHEAR RATE (sec ⁻¹)						
		1.15	2.30	5.74	11.5	23.0	46.0	115.0
55	Cellosolve Acetate	28	30	43	36	37	37	
	1,4 dioxane	70	48	46	40	38	38	
	MIBK	30	40	34	38	39	39	
	MEK	20	26	22	16	16	17	16
	n-butyl acetate	30	55	42	37	36	35	
	THF		28	25	22	23	21	
	ethylacetate	60	48	32	25	22	19	19
65	Cellosolve Acetate	90	115	100	95	95		
	1,4 dioxane	126	105	97	94	88		
	MIBK	130	115	103	95	94		
	MEK	90	69	52	50	48	46	
	n-butyl acetate	140	113	95	90	87		
	THF	190	165	146	134			
	ethylacetate	100	80	51	57	54	50	
75	Cellosolve Acetate	290	265	246				
	1,4 dioxane	370	315	282				
	MIBK	300	265	243				
	MEK	190	168	155	145			
	n-butyl acetate	246	235	223				
	THF	216	203	183	168			
	ethylacetate	247	219	218	186			
85	Cellosolve Acetate	706	705					
	1,4 dioxane	810	805					
	MIBK	793	830					
	MEK	600	577					
	n-butyl acetate	706	710					
	THF	520	483					
	ethylacetate	546	510					

*The concentrations are in percent volume solids based on the calculated volumes of the unmixed components. The viscosity was measured on a Wells-Brookfield Micro Viscometer at 298°K (77°F).

Table 6

L-2291 Solution Viscosity*

Volume Concentration	Solvent	Shear Rate (sec. ⁻¹)					
		1.15	2.30	5.74	11.5	23.0	46
65	Cellosolve Acetate			50	46	45	44
	1,4 dioxane			47	46	45	44
	MIBK			40	38	38	37
	MEK			27	25	23	22
	n-butyl acetate			47	42	42	41
	THF			44	37	37	34
75	Cellosolve Acetate	170	133	111	106		
	1,4 dioxane		100	90	94	94	
	MIBK		110	95	90	88	
	MEK		83	64	57	54	
	n-butyl acetate	150	123	107	101		
	THF		96	80	78	75	

* The concentrations are in percent volume solids based on the calculated volume of the unmixed components. The viscosity was measured on a Wells-Brookfield Micro Viscometer at 298°K (77°F).

ranked second in ability to yield solutions of minimum viscosity.

3. Titanium Dioxide Dispersions

The viscosities of several of the TiO_2 pigment dispersions in the candidate polyols have been measured using the Haake Rotovisco. Examples of the viscosity profiles generated are presented in Figures 17 and 18. The duplicate curves seen there were generated by starting at high shear rate, incrementally decreasing the shear rate to its minimum value and then progressively increasing the shear rate back to the initial value.

Qualitatively, the rheological behavior of the Acryloid AU-568 systems is different than the rheological behavior of the Cargill 5760 systems. The higher yields in the Acryloid AU-568 based dispersion reflect the better low shear viscosity of these dispersions in comparison to the Cargill 5760 systems. The Cargill 5760 based dispersions give the impression of having a gel like structure when stirred with a spatula.

The magnitude of the subjective difference between the Acryloid AU-568 and the Cargill 5760 is not fully reflected in the viscosity profiles generated and given in Figures 17 and 18. The profiles for the two systems at the same volume solids (55% and 60%) show the Cargill 5760 system to have a lower measured viscosity than the Acryloid AU-568 except at low shear rates. The shear thinning (pseudoplasticity) of the Cargill 5760 systems is quite evident. Only the 55 percent

volume solids dispersion for the Acryloid AU-568 system shows much dependence of its viscosity on shear rate. It should be noted that pigmented systems using the Acryloid AU-568 and the Cargill 5760 blended with Desmodur N-100 have been successfully sprayed at 65 percent volume solids. The viscosity differences observed so far appear not to be critical for conventional spray application.

Casson plots of the viscosity-shear rate data were made for the TiO_2 dispersion in Acryloid AU-568, Cargill 5760, and NIAX PCP-0300. These plots are given in Figures 19, 20, and 21. All the materials gave linear curves except the TiO_2 / Acryloid AU-568 system at 55 percent volume solids. The reasons for the unexpected behavior are not known.

The data used to draw the Casson plots were also used to fit the rheological information to the Casson equation -

$$\eta^{1/2} = \eta_{\infty}^{1/2} + \tau_0^{1/2} \gamma^{-1/2} \quad (4)$$

where η is the viscosity in centipoise, η_{∞} is the infinite shear rate viscosity in centipoise, τ_0 is deemed the yield stress and has units of dynes/cm², and γ is the shear rate with units of sec⁻¹. The η_{∞} parameter is used as a measure of the viscosity of a material for the shear rates encountered in spraying, brushing, and rolling. The range of η_{∞} for proper atomization in spraying has been given as 40 ops to 150 ops.

The good low shear viscosity of the Acryloid AU-568 systems (high ball mill discharge yields) is reflected in the low values of the yield stress in comparison to the Cargill

5760 and NAX PCP-0300 systems. More interesting, however, is the observation that the η_{sp} values do not show the wide range in magnitude like τ_0 . All the η_{sp} values are within the range of "sprayable" viscosity. Both τ_0 and η_{sp} are increasing functions of concentration. For comparison, τ_0 and η_{sp} for the control pigmented base, 821 X 330, are 3.2×10^{-1} dynes/cm² and .467 cps, respectively.

A Casson plot using viscosity-shear rate data collected on the pigmented base DeSoto 821 X 330 Super Desothane Aliphatic Polyurethane Enamel White No. 17875 using the plate and cone arrangement on the Haake Rotovisco did not yield a straight line as expected. It was surmised that the viscosities measured were higher than the true dispersion viscosities since the pigment particles were larger than the minimum gap between the plate and cone, leading to a high, misleading torque in the measuring system. A Casson plot of the viscosity data measured with the bob and cup attachment of the Haake Rotovisco did give a straight line. The gap in this measuring unit is much larger than the maximum gap in the plate and cone unit. The lower dispersion viscosities and the linear Casson plot of the viscosity data (Figure 22) is supportive to the conjecture of false readings of viscosity for pigmented systems on the plate and cone apparatus.

The reason behind the superior performance of the Acryloid AU-568 in the dispersion preparations is not known. All the materials evaluated, with the exception of the Acryloid AU-568,

are hydroxy functional. This may result in some acid-base type interactions between the hydroxyl groups and the amphoteric surface of the TiO_2 which undoubtedly has absorbed water on its surface. No attempt was made to vigorously exclude water from the materials used so there is the possibility that the oxazolidine group of the Acryloid AU-568 is opened to some extent in the dispersion to yield a secondary hydroxy group and a secondary amine, both of which are good groups for dispersion durability. The exact situation is complicated. Water was intentionally added to the grind formulation (2289-103) at an oxazolidine/water equivalents ratio of one to see if the viscosity would be affected in any significant way. Based on the yield of 2289-103 compared with one in which no water had been added, no difference was observed. However, the equilibrium composition in the oxazolidine-water reaction favors the oxazolidine group so that insufficient water may have been present to force the opening of a large fraction of the oxazolidine groups.

B. Film Formation

1. Clear Films

The polyols were formulated at two NCO/OH levels: 2 and 1.25. These levels were initially selected to determine the effect of crosslink density on the final film properties. Closer analysis of the crosslink density revealed that the crosslink density was relatively insensitive to the NCO/OH ratio in formulations where the polyol had a functionality

of three or greater. The crosslink density was calculated by determining the weight of polymer in the film per mole of crosslinks, W_c . For these calculations, the polyisocyanate, Desmodur N-100 or Desmodur N-75, was taken as trifunctional. When the polyisocyanate is blended with a diol, the value of the average molecular weight per mole of crosslinks is

$$W_c = \frac{3(S \cdot E_{NCO} + E_{OH})}{S} \quad (5)$$

If the polyol has a functionality greater than two, the expression for W_c is

$$W_c = \frac{3f(S \cdot E_{NCO} + E_{OH})}{3 + fS} \quad (6)$$

In these expressions, E_{NCO} is the isocyanate equivalent weight, E_{OH} is the hydroxyl equivalent weight of polyol, S is the NCO/OH ratio, and f is the functionality of the polyol. This analysis shows that the crosslink density for most of the films has remained fairly constant even though the NCO/OH ratio was varied: the property that is changing the most is the composition of the polymer film as measured by the weight fraction of Desmodur N-100 in the film.

From the data accumulated, three formulations exhibited physical and chemical properties close to the program goals: Acryloid AU-568, Cargill 5760, and NIAx Caprolactone PCP-0300.

These polyols appear promising for further development into high solids coating systems. The Acryloid AU-568 has many of the desirable properties for the high solids coating system plus acceptable pot life characteristics since the reaction between the isocyanate group and the oxazolidine group requires the presence of water. Reasonable precautions against the inclusion of water in the formulation, as is normal practice for two package, isocyanate systems, is expected to yield pot life times in excess of the 7.2 ks (2 hr.) called for in the specifications.

2. Pigmented Films

The spray application characteristics of the pigmented polyols are given in Table 7. The volume solids presented there are not the maximum solids at which the paints can be sprayed. The volume solids used were chosen to be more attractive from the standpoint of higher solids than conventional systems and to lend some assurance of obtaining films for testing. It is felt that, after handling the systems in Table 5 at the specified volume solids, all the systems would apply adequately near the program target of 65% volume solids with conventional spray equipment.

The impact flexibility properties of the NIAX PCP-0300 systems equal the good performance of the control systems, passing 60% elongation for both room temperature conditioned films and the heat stability test films. Pigmentation of the Cargill 5760 at the 25% PVC level drastically reduced the impact

Table 7

Candidate Polyol Application Characteristics

Material	Formulation	WCO/CH	PVC Volume (%) Solids	Weight (%) Solids	#2 Zahn Cup Solvent Viscosity	Appearance/Comments
Arpiaz K6030-A1-80	2248-183A	2	-	54	WEX	Desmodur N-100 used; margins: atomization at 2.8 kg/cm ² (40 psi); air bubbles, turbidity in wet films; Orange peel effect in film sprayed at 2.8 kg/cm ² (40 psi) but smooth film when sprayed at 3.8 kg/cm ² (55 psi).
Arpiaz K6030-A1-80	2248-183B	2	-	54	WEX	Desmodur N-100 used; good atomization at 2.8 kg/cm ² (40 psi) and 3.5 kg/cm ² (50 psi); air bubbles, turbidity in wet films but much less than 2248-183A.
Arpiaz K6030-A1-80	2248-187A	2	-	55	WEX	Desmodur N-100 used
Arpiaz K6030-A1-80	2248-187B	1.25	-	55	WEX	Desmodur N-100 used
Carbail 5760	2248-192A	2	25	51	WEX	L-2291 used Both atomize at 3.5 kg/cm ² (50 psi); no detectable difference in spray properties; orange peel in wet film
Carbail 5760	2248-192B	2	25	51	WEX	Desmodur N-100

Table 7 (Cont'd)

Material	Formulation	HCO/0H (%)	PVC Volume Solids (%)	Weight Solids (%)	Solvent (%)	#2 Zahn Cup Viscosity	Appearance/Comments
Acryloid A3-566	2248-192C	2	25	64	80	MEK	L-2291 Both spray well at 3.5 kg/cm ² (50 psi); no detectable difference in spray properties.
Acryloid AU-566	2248-192D	2	25	64	80	MEK	Desmodur N-100
MIAX PCP-0300	2248-192E	2	18	60	75	MEK	L-2291 Both spray at 3.5 kg/cm ² (50 psi); no detectable difference in spray application; orange peel in wet film.
MIAX PCP-0300	2248-192F	2	18	60	75	MEK	Desmodur N-100
Acryloid AU-566	2248-194A	2	25	64	80	MEK	26s @ 299°F (78°F) L-2291
Cargill 5760	2248-194B	2	25	65	81	MEK	45s @ 295°F (72°F) L-2291
MIAX PCP-0300	2248-196A	2	18	60	75	MEK	25s @ 296°F (74°F) L-2291
MIAX PCP-0300	2248-196B	1.25	18	60	75	MEK	L-2291; insufficient material to measure viscosity

properties in comparison to the data for the unpigmented Cargill 5760: 2-5% versus 60% (room temperature) and 20% versus 40% (heat stability). The films with Acryloid AU-568 also had poorer impact flexibility when pigmented: 1-2% versus 20% (room temperature) and 5% versus 20% (heat stability). The low temperature flexibilities of the candidate systems are poor. The best system up to this point, PCP-0300/Desmodur N-100, passed the test at 25.4 mm (1 inch) but failed at 12.7 mm (1/2 inch). Unpigmented films of the PCP-0300/Desmodur N-100 were earlier found to pass the 12.7 mm (1/2 inch) bend at NCO/OH = 2 and to pass the 11.11 mm (7/16) bend at NCO/OH = 1.25. Pigmentation has severely reduced the low temperature flexibility of these materials.

The Cargill 5760, Acryloid AU-568, and the NIAX PCP-0300 coatings, all at NCO/OH = 2, give good fluid resistance performance. The presence of the TiO_2 in the Cargill 5760/Desmodur N-100 polymer matrix appears to have increased the resistance to Skydrol 500B: unpigmented, the films soften from an original HB hardness to less than a 4B pencil; pigmented, the film dropped only two pencil hardness units, from F to B. For the Acryloid AU-568 based coating, the pigmented films are less sensitive to the hydrocarbon fluid since no softening was detected while the unpigmented film softened from HB to 2B. The fluid resistance properties associated with NIAX PCP-0300/Desmodur N-100 films (no softening in any of the test fluids at NCO/OH = 2) have been maintained in the pigmented films. It is interesting to note that the Acryloid AU-568/Desmodur N-100

materials at $\text{NCO/OH} = 0.7$ did not disasterously fail the fluid resistance tests despite the stoichiometric imbalance.

Data on the durability tests of salt spray resistance, humidity resistance, and accelerated weathering for pigmented systems indicates no loss of adhesion, blistering, or corrosion in the salt spray and humidity exposures. The accelerated weathering test does show some degradation. All the systems have a lower gloss after the 1.8Ms exposure (500 hour) and slight embrittlement of film properties. The Acryloid AU-568 shows the greatest decrease in gloss (10 percent relative decrement).

3. Polyisocyanate Substitution

Previous work in this program comparing the solution viscosity of the experimental polyisocyanate L-2291 (Mobay Chemical Corporation) with the Desmodur N-100 polyisocyanate demonstrated that the L-2291 solutions were approximately one-half as viscous as the Desmodur N-100 solutions at the same concentrations and in the same solvents.

Contrary to expectations, little if any difference was noted in the atomization of several systems using the L-2291 in contrast to the Desmodur N-100. Although viscosities were not measured, handling of the blended systems indicated that the viscosity of the formulations was dominated by the viscosity of the pigment dispersion. The Acryloid AU-568 dispersion was lower in viscosity than the NIAX PCP-0300 and Cargill 5760 dis-

persions. Atomization and flow in both the L-2291 and Desmodur N-100 blends with Acryloid AU-568 were excellent. Both the Cargill 5760 and the NIAX PCP-0300 based systems were thixotropic. Atomization was adequate but the wet films as well as the cured films have an orange peel effect.

In comparison to coatings using Desmodur N-100, the performance with L-2291 is very similar. The major improvement is in the low temperature flexibility test in the NIAX PCP-0300 coatings. The fluid resistance properties of the L-2291 coatings still do not meet the program requirements.

A diisocyanate from General Mills, DDI 1410, was also evaluated. It was felt that the use of a diisocyanate in the Acryloid AU-568 formulations would help the low temperature flexibility. The Acryloid AU-568 tends to form very brittle, inflexible films.

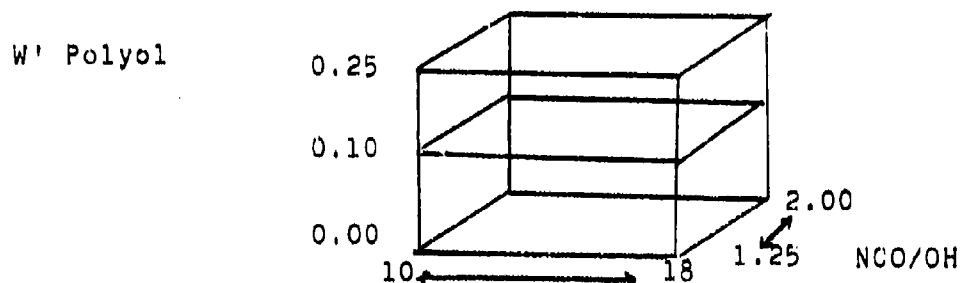
The Acryloid AU-568/DDI 1410 films (pigmented) show excellent improvement in low temperature flexibility. The impact flexibility was also excellent, at least equaling the performance of the control coating. It should be noted here that the high level of isocyanate material in these films corresponds to the lower crosslink density films.

The fluid resistance of the films using DDI 1410 is marginal. Some resistance to softening in water is exhibited.

C. Formulation Modification

1. Polyols

In earlier work it was found that pigmentation of a polyol/polyisocyanate combination degraded the low temperature flexibility and impact properties in comparison to the unpigmented film. Included, therefore, in the initial evaluation of polyol blends with the Desmodur N-100 was variation of the pigment volume concentration, PVC. The experimental design involved a three level, eight factor cubic. This may be shown as indicated below.



In general, the replacement of a portion of the Acryloid AU-568 with the oligomeric diols improves the impact flexibility properties, both at room temperature and after heat aging, but decreases fluid resistance.

One formulation (2408-9) exhibits performance properties, both physical and chemical, which closely approximate the program goals.

Table #8

Formulation 2408-9 Composition

<u>Material</u>	<u>Weight Percent</u>	<u>Volume Percent</u>
TiO ₂	20.93%	6.40%
Acryloid AU-568	17.74	19.95
NIAX PCP-0300	5.91	6.47
Desmodur N-100	34.05	35.63
MEK - Urethane Grade	20.79	31.00
Dibutyl tin dilaurate	0.58	0.55

PVC = 10%
NCO/OH = 1.77

Performance properties of formulation 2408-9 are listed in Table 9.

Modification of the NIAx PCP-0300/Desmodur N-100 and Cargill 5760/Desmodur N-100 resulted in films with poor overall physical and chemical properties.

2. Polyisocyanate Blends

The incorporation of the DDI 1410 or L-2291 into the Aeryloid AU-568/Desmodur N-100 systems results in some improvement in the impact flexibility properties in comparison to the equivalent, straight Desmodur N-100 coating. The improvement is not large and similar impact flexibility increases have been observed in the oligomeric diol studies, i.e. ~5 percent elongation to ~10-20 percent elongation. The fluid resistance of these formulas still fall short of the program expectations.

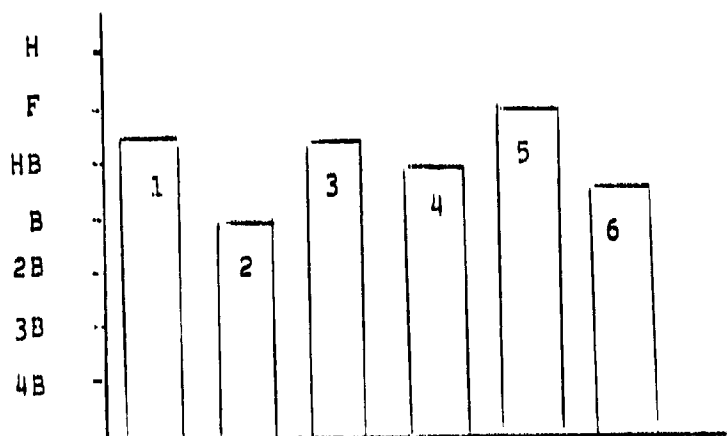
D. Airless Electrostatic Spray

The formulations evaluated were applied by conventional air spray techniques at a pressure of 35 kg/cm² (50 lb/in²). The program requirements specify application by airless electrostatic spray. When applied by this method, the "best" formulation developed to date (2408-9) exhibits acceptable atomization with a small degree of fingering (streams of unatomized material) appearing at the top and bottom of the fan. Considerable foaming and sagging is noted in the formed films.

Table 9

Performance Properties of Formulation 2408-9

Composition	Acryloid AU-568/NIAX PCP-0300/Desmodur N-100
Viscosity (#2 Zahn Cup)	28 seconds
Spray Characteristics	Sprays well with slightly coarse atomization-good leveling.
Impact Flexibility	40%*
High Temperature Stability-Impact Flexibility	40%*
Low Temperature Flexibility-Straight Mandrel	25.4 mm (1 in)
60° Gloss	93
5% Salt Spray Resistance	Small blisters formed
100% Relative Humidity	Small blisters formed
Fluid Resistance	



1. Initial pencil hardness.
2. Pencil hardness after 24 hour immersion in lubricating oil at 250°F.
3. Pencil hardness after 7 day immersion in hydrocarbon fluid.
4. Pencil hardness after 7 day immersion in hydraulic fluid.
5. Pencil hardness after 7 day immersion in Skydrol 500B fluid.
6. Pencil hardness after 4 day immersion in water (100°F).

These phenomena may be attributable to the high pressures necessary for spraying. The coating does have a tendency to "wrap" around the panel. This further decreases environmental pollution by eliminating overspraying.

E. Glass Transition Temperature Correlations

The second order or glass transition temperature, T_g , is a characteristic property of polymers and convenient as a method of comparison. This is the temperature at which an amorphous material changes from a brittle glassy state to a rubbery state and is measured as the abrupt change in slope of the plot of some physical property (e.g. refractive index, specific volume, flexural modulus) against temperature. While T_g may not be recognized as being critical in coatings applications, it bears a direct relationship to such important properties as hardness, elongation, and flexibility.

T_g values were determined by differential scanning calorimetry (DSC) for the high solids coatings systems evaluated. Data for the Acryloid AU-568/NIAX PCP-0300/Desmodur N-100 blending series may be found in Table 10 & 11. A trend of increasing flexibility with decreasing T_g is evident in figures 23 and 24, as was expected.

No direct correlation between T_g values and the other performance properties is noted. A possible explanation for the lack of dependence of fluid resistance on T_g is

that fluid resistance is actually the resistance to chemical degradation of the formed films, and not related to the physical properties of the polymer unit.

TABLE 10
PERFORMANCE PROPERTIES OF ACRYLOID AU-568/MIAX PCP-0300/DESMODUR K-100 HIGH SOLIDS SYSTEMS

FORMULATION (2408-)	PVC (%)	WCO/OH	PCP-0300	FILM THICKNESS (mm(in.))	ROOM TEMPERA- TURE IMPACT FLEXIBILITY (%)	HIGH TEMPERA- TURE STABILITY IMPACT FLEXI- BILITY (%)	LOW TEMPERA- TURE FLEXI- BILITY STRAIGHT PANDREL (mm(in.))	GLOSS (60°)
17	10	1.24	0.00	43.2(1.7)-76.2(3.0)	10-20	20	> 25.4(1)	91
6	10	1.18	0.10	45.7(1.8)-81.3(3.2)	20	20	> 25.4(1)	91
10	10	1.1	0.25	50.8(2.0)-94.0(3.7)	40	40	> 25.4(1)	91-92
12	10	2.0	0.00	43.2(1.7)-76.2(3.0)	10-20	20-40	25.4(1)	91-92
16	10	1.91	0.10	45.7(1.8)-76.2(3.0)	20-40	20	> 25.4(1)	91-92
9	10	1.77	0.25	55.9(2.2)-86.4(3.4)	40	40	25.4(1)	93
18	18	1.25	0.00	35.6(1.4)-71.1(2.8)	5-10	5-10	> 25.4(1)	91-92
19	18	1.19	0.10	50.8(2.0)-94.0(3.7)	5-10	20	> 25.4(1)	91-92
7	18	1.11	0.25	48.3(1.9)-114.3(4.5)	40	20	> 25.4(1)	92
8	18	2.01	0.00	53.3(2.1)-94.0(3.7)	10	10	> 25.4(1)	92-9
11	18	1.69	0.10	48.3(1.9)-83.8(3.3)	5-20	10	> 25.4(1)	93
13	18	1.77	0.25	53.3(2.1)-81.3(3.2)	20-40	20-40	> 25.4(1)	91-92
6C		---	---	48.3(1.9)-81.3(3.2)	60	60	> 25.4(1)	91
821x330/910x376								

a. Resistance to test fluids is indicated by decrease in pencil hardness units.
See Appendix

TABLE 11
FLUID RESISTANCE PROPERTIES OF ACRYLOID AF-568/MIAX PCP-0300/DESMODUR N-100 HIGH SOLID SYSTEMS

FORMULATION (2408-)	PVC (%)	MCO/OH	W/PCP- 0300	FILM THICKNESS (mm (in.))	INITIAL PENCIL HARDNESS	LUBRI- CATING OIL	HYDRO- CARBON FLUID	HYDRAULIC FLUID	SYNDRON 500B	H ₂ O ^a	T _g (°C)
17	10	1.24	0.00	43.2(1.7)-76.2(3.0)	HB	2	1	0	0	0	51
6	10	1.18	0.10	45.7(1.8)-81.3(3.2)	HB	1	2	0	0	1	41
10	10	1.1	0.25	50.8(2.0)-94.0(3.7)	HB	2	2	0	1	2	19
12	10	2.0	0.00	43.2(1.7)-76.2(3.0)	HB	2	0	0	0	0	65
16	10	1.91	0.10	45.9(1.8)-76.2(3.0)	F,HB	2	0	9	0	1	56
9	10	1.77	0.25	55.9(2.2)-86.4(3.4)	F,HB	1	0	0	0	1	49
18	18	1.25	0.00	35.6(1.4)-71.1(2.8)	P	3	2	0	0	1	41
19	18	1.19	0.10	50.8(2.0)-94.0(3.7)	P	3	2	0	0	1	38
7	18	1.11	0.25	48.3(1.9)-114.3(4.5)	P	1	3	1	1	2	24
2	18	2.01	0.00	53.3(2.1)-94.0(3.7)	2H,F	2	2	0	1	1	62
11	18	1.60	0.10	48.3(1.9)-83.8(3.3)	2H	3	3	1	2	3	58
13	18	1.77	0.25	53.3(2.1)-81.3(3.2)	F	2	1	1	0	0	39
Control 6C	—	—	—	48.3(1.9)-81.3(3.2)	HB	0	2	0	H	2	9

IV. Conclusions

A number of significant conclusions have been obtained from this study. Basically, the attainment of the primary goal of producing a 65% high volume solids, two-package, urethane topcoat meeting the requirements of MIL-C-83286 for military applications appears ultimately feasible. However, additional effort is required to totally realize this goal. The pot life of the mixed two-package system and the spray viscosity of the final formulation have been found to be significant problems. The resolution of these difficulties through the utilization of oxazolidine functionality on the polyol component is anticipated.

Additionally, significant aspects of the technology of high solids coatings have been explored. These new developments and conclusions are summarized below.

1. Potential polyol and polyisocyanate candidates may be screened via construction of concentration-viscosity diagrams. Development of this technique should enhance its use as a routine laboratory screening tool for the selection of high solids formulations components.
2. The rheological behavior of these concentrated solutions was unexpected. The choice of solvent appears to contribute to the solution rheology to a greater extent than predicted.

3. The typical polyol-polyisocyanate prepolymer components cure too rapidly in high solids formulations. Techniques to retard the rapid curing reactions, or complete substitution of one of the components will have to be developed to render these formulations practical.
4. The formulations containing oxazolidine prepolymers have exhibited increased pot life properties and have closely approximated the program goals.
5. An enhanced qualitative understanding of high solids systems have resulted from theoretical calculations. Because the application of these techniques is in an incipient phase, a complete understanding of the results will require additional experimental data.
6. Conventional air spray techniques appear at this time not to be completely practical for high solids systems. Control of final viscosity over a period of two hours (projected pot life) is a major concern with the use of the present component prepolymers.

V. Future Work

A. Materials Screening

1. An effort should be made to obtain the proper blend of materials (polyol and isocyanates) which meets the full range of performance requirements.

2. An on-going review of the commercial products literature should be made in order to identify possible new polyol candidates.

3. Particular emphasis should be directed towards the development of Desmodur and L-2291 systems because these prepolymers appear to yield the best formulations approaching the program goals.

B. Reactive Diluents

The use of reactive diluents in coatings formulation for High Solids application is an area of currently active research in the coatings industry. The reactive diluents which would most probably give the best results in Table 12.

Table 12

Reactive Diluents

<u>Material</u>	<u>Functionality</u>
1,2-Ethanediol (Ethylene glycol)	2
1,2-Propanediol (Propylene glycol)	2
1,6-Hexanediol	2
1,3-Propanediol	
2-Ethyl, 1,3-Hexanediol	2
2,2'-Dihydroxy Diethylether (Diethylene Glycol)	2
1,4-Butanediol	
Trimethylol propane	3
Pentaerythritol	4
Pluracol Polyether Diols (BASF Wyandotte)	2
Pluracol Polyether Triols (BASF Wyandotte)	3
Pluracol Polyether Tetrols (BASF Wyandotte)	4
Caprolactone Polyols (Union Carbide)	2, 3, 4, 6

C. Pigmentation

The best candidate formulation should be pigmented to match the Federal Color Standard 595. Five pigments should be considered.

No. 34102	Light Green
No. 36622	Aircraft Gray
No. 34079	Dark Green
No. 30219	Tan
No. 17875	Insignia White

D. Application

In addition to conventional air spray, evaluation of various application techniques should be made. The feasibility of using an airless electrostatic spray system should be extensively considered.

Because of the shortness of pot life of a number of the polyol prepolymer systems evaluated, the possibility of "Mix-in-Head" gun application exists. In the event the final formulation has a short pot life, this type of application should be investigated.

E. Oxazolidine Chemistry

With the goal of extending and improving the systems containing oxazolidine components, more effort will be made to further develop this formulation concept. Rohm and Haas offers other oxazolidine based prepolymers for use with polyisocyanates. These materials (such as AU-528) should be evaluated in a continuation program. In addition, a number of oxazolidine prepolymers have been prepared in the DeSoto

laboratories, and these materials will also be evaluated in final formulations. These evaluations will parallel an in-house program to synthesize new oxazolidine for use in coating systems.

F. Glass Transition Temperature Correlations

The correlation of performance properties with T_g values of the final formulations should be continued. Specifically, the importance of the ratios of the blend components should be further investigated. Plots of T_g values versus specific properties should be made, and observed trends will be further exploited.

G. Theoretical Considerations

One of the most general equations for estimating the viscosity of a liquid containing spherical particles is that proposed by Mooney in 1951. The degree of applicability of this theoretical equation to the present investigation should be determined.

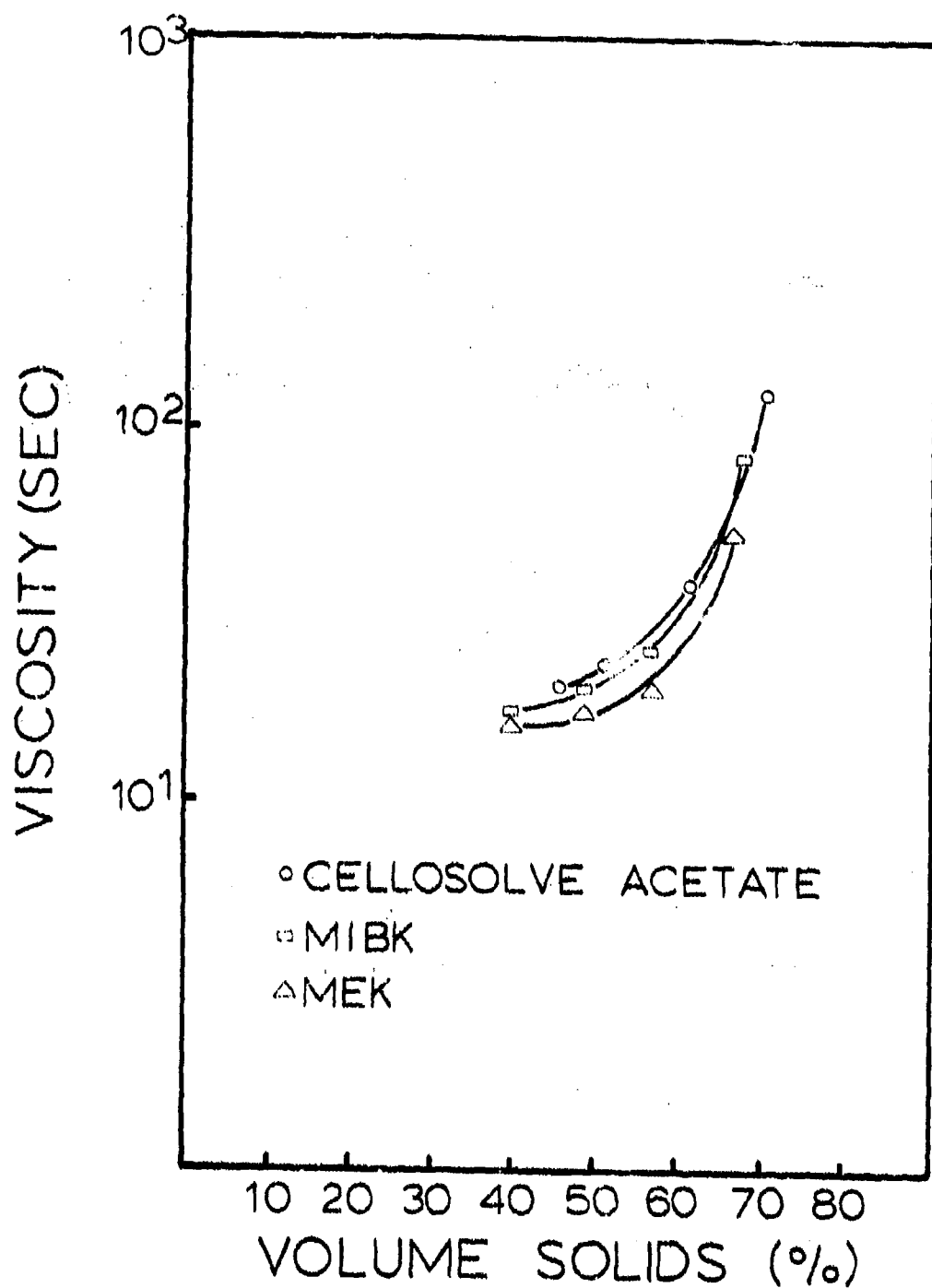


Figure 1. Acryloid AU-568 Solution Viscosities
#2 Zahn Cup 298°K (77°F)

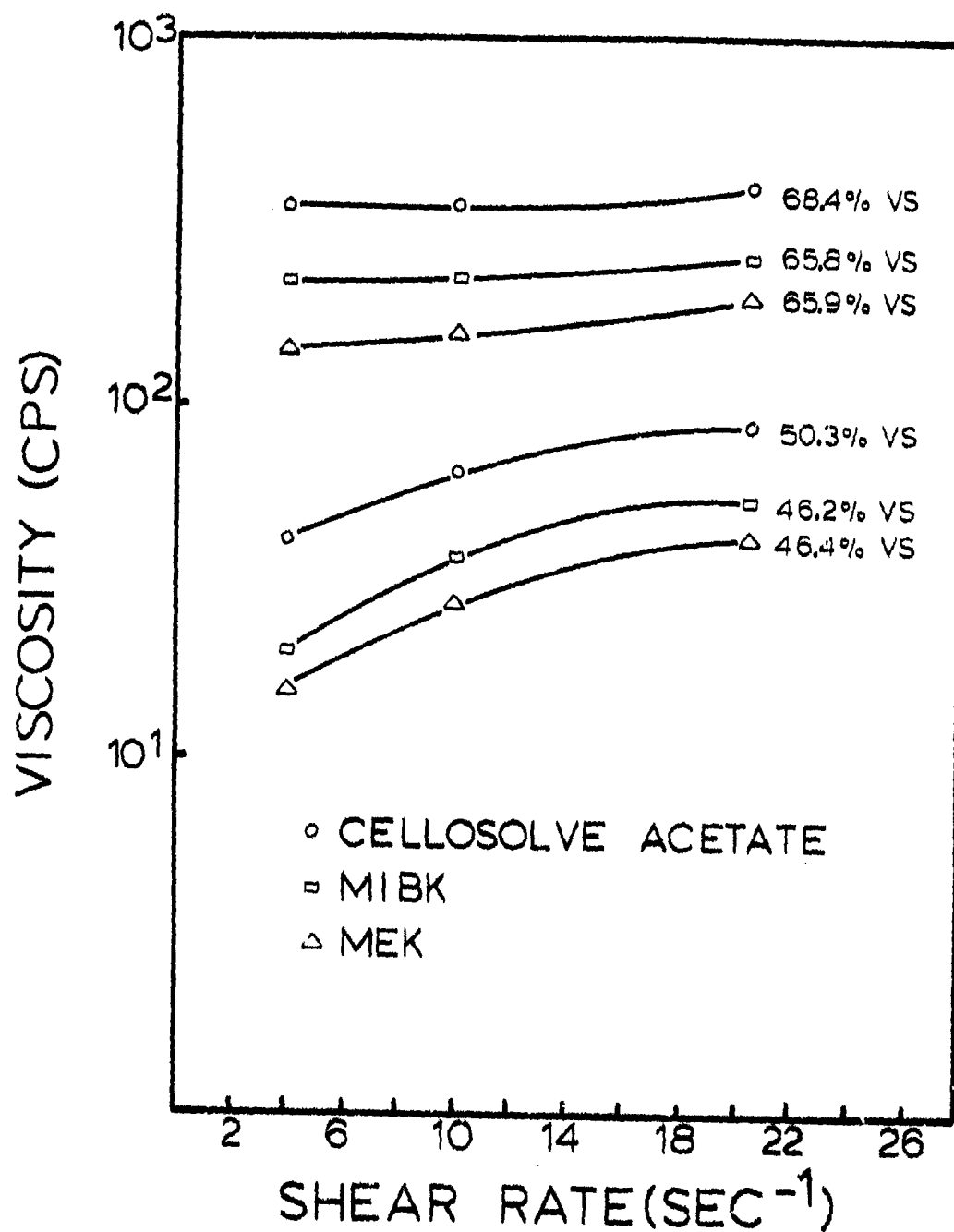


Figure 2. Acryloid AU-568 Rheogram
 Brookfield Synchro-Lectric
 #2 Spindle, 298°K (77°F)

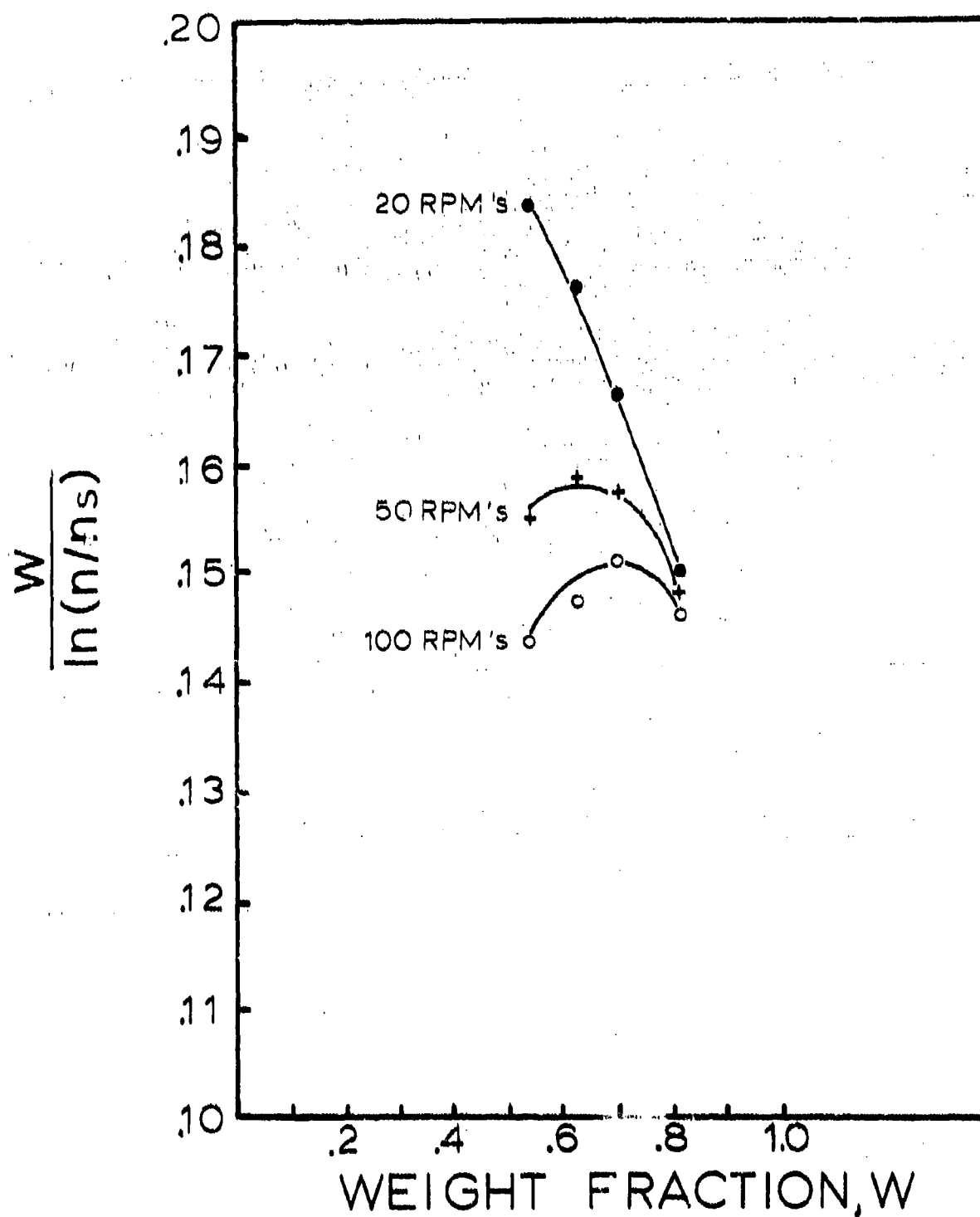


Figure 3. Acryloid AU-568/Cellosolve Acetate Erickson Plot
 Brookfield Synchro-Lectric #2 Spindle
 298°K (77°F)

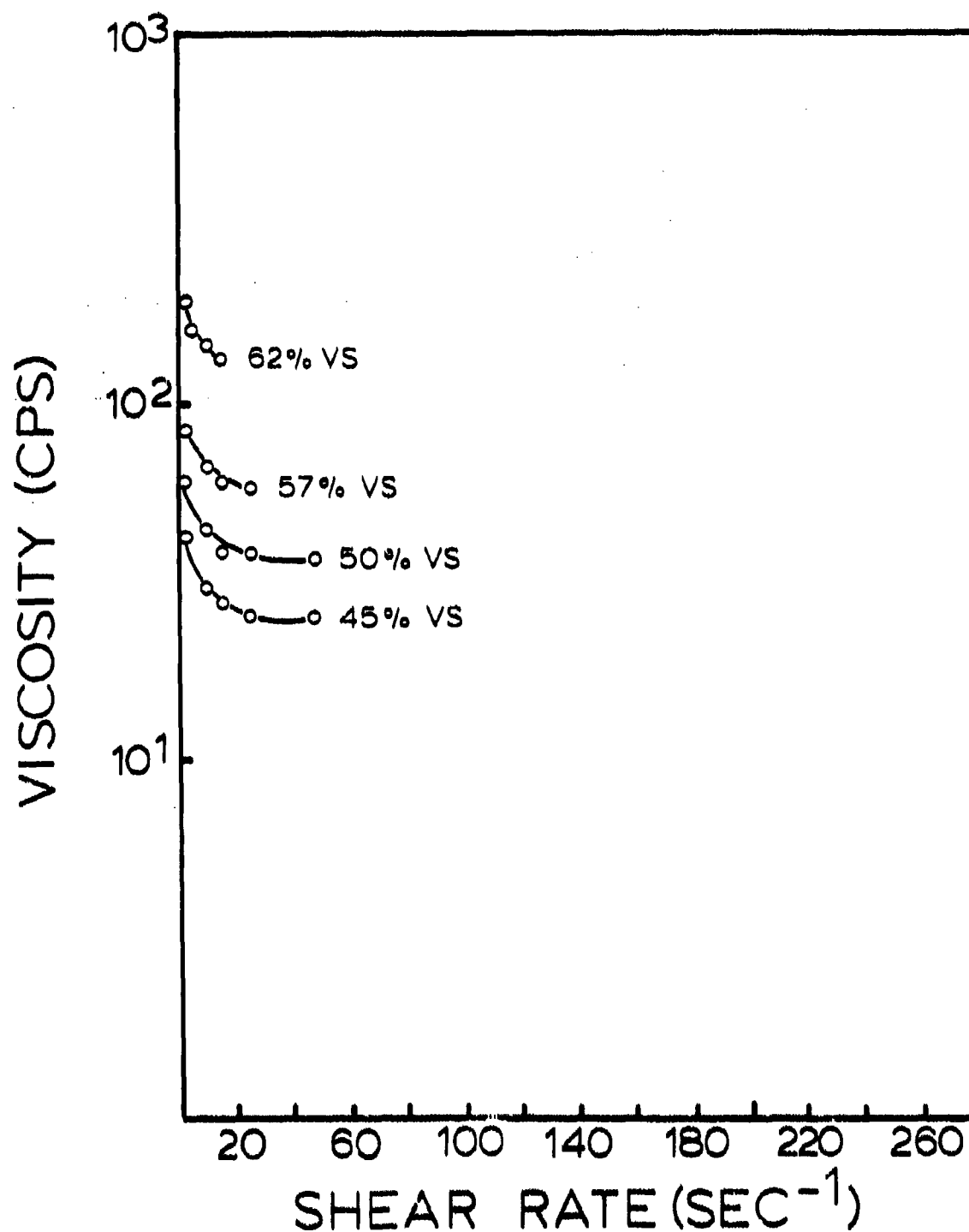


Figure 4. Acryloid AU-568/Cellosolve Acetate Rheogram
Wells-Brookfield 298°K (77°F)

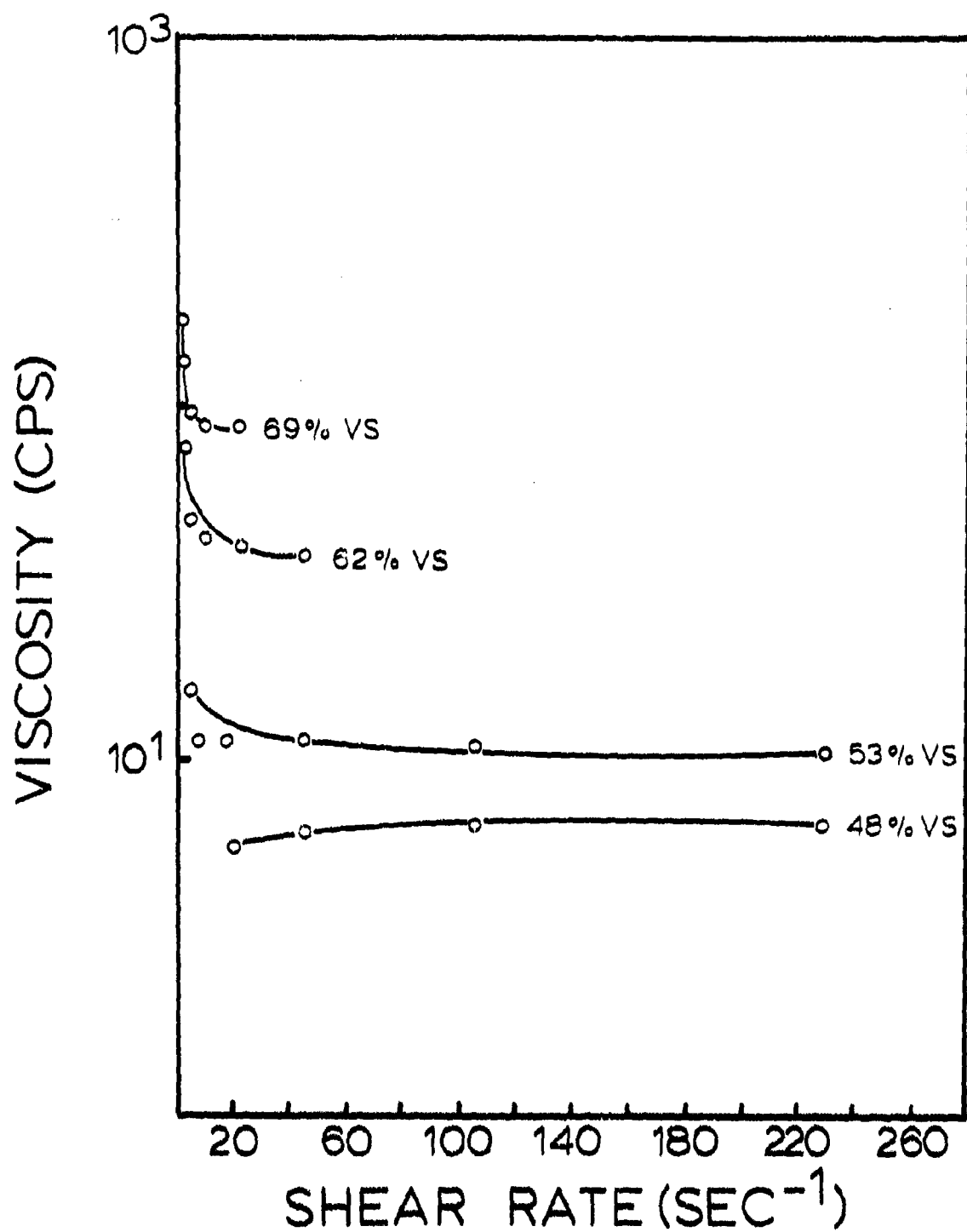


Figure 5. Acryloid AU-568/MEK Rheogram
Wells-Brookfield 298°K (77°F)

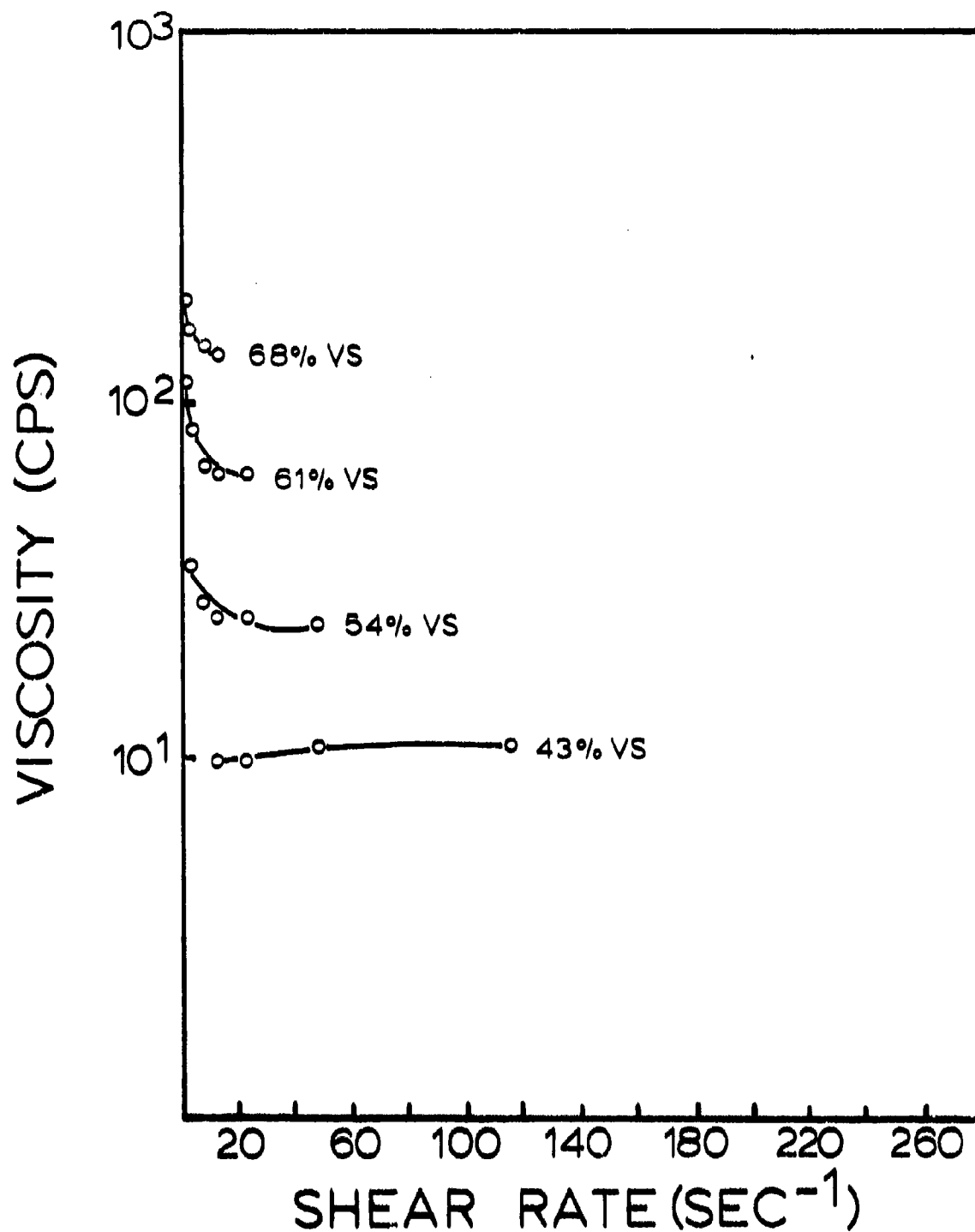


Figure 6. Cargill 5760 Rheogram

Wells-Brookfield 298°K (77°F)

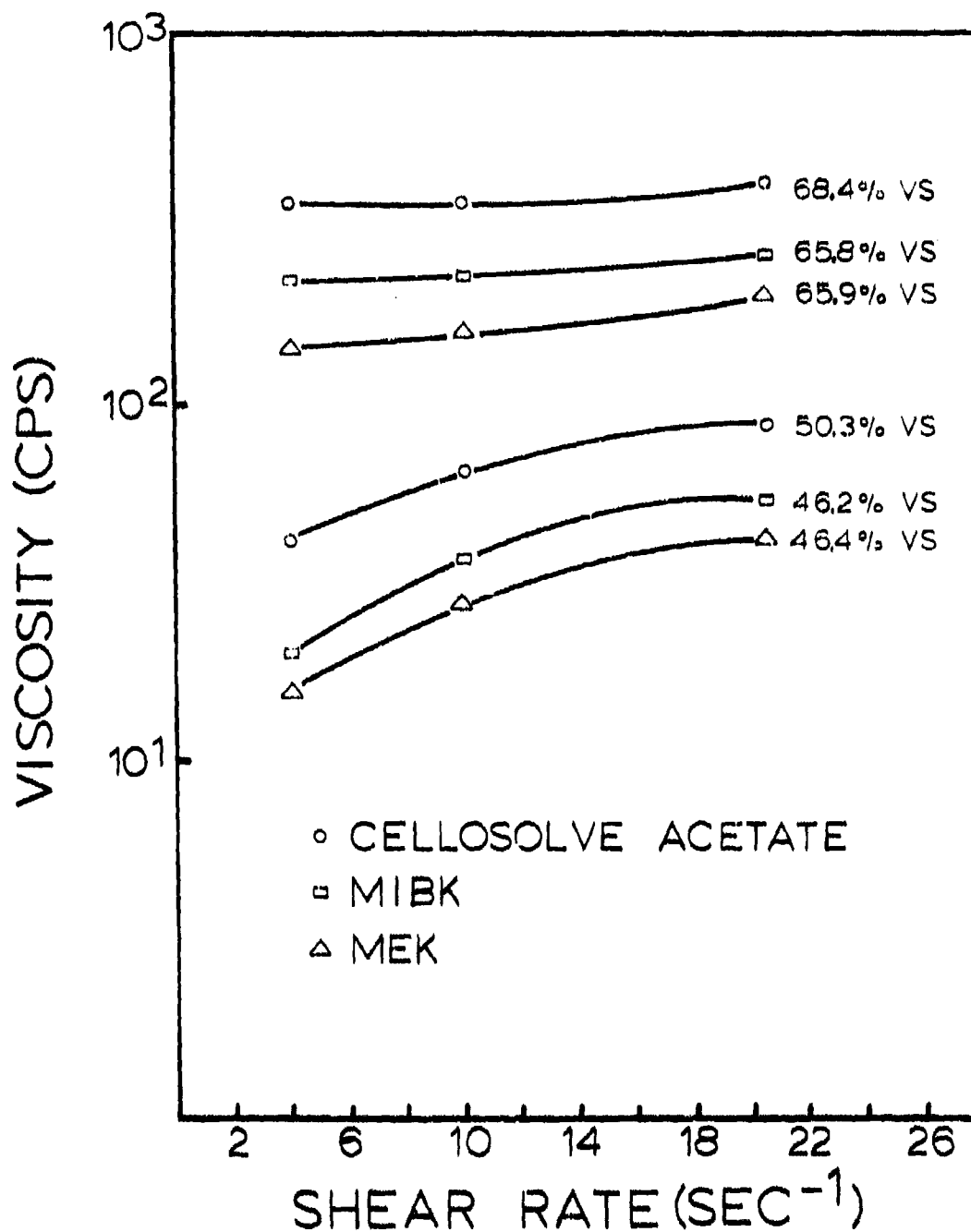


Figure 7. Acryloid AU-56B Rheogram
Brookfield Synchro-Lectric
#2 Spindle 298°K (77°F)

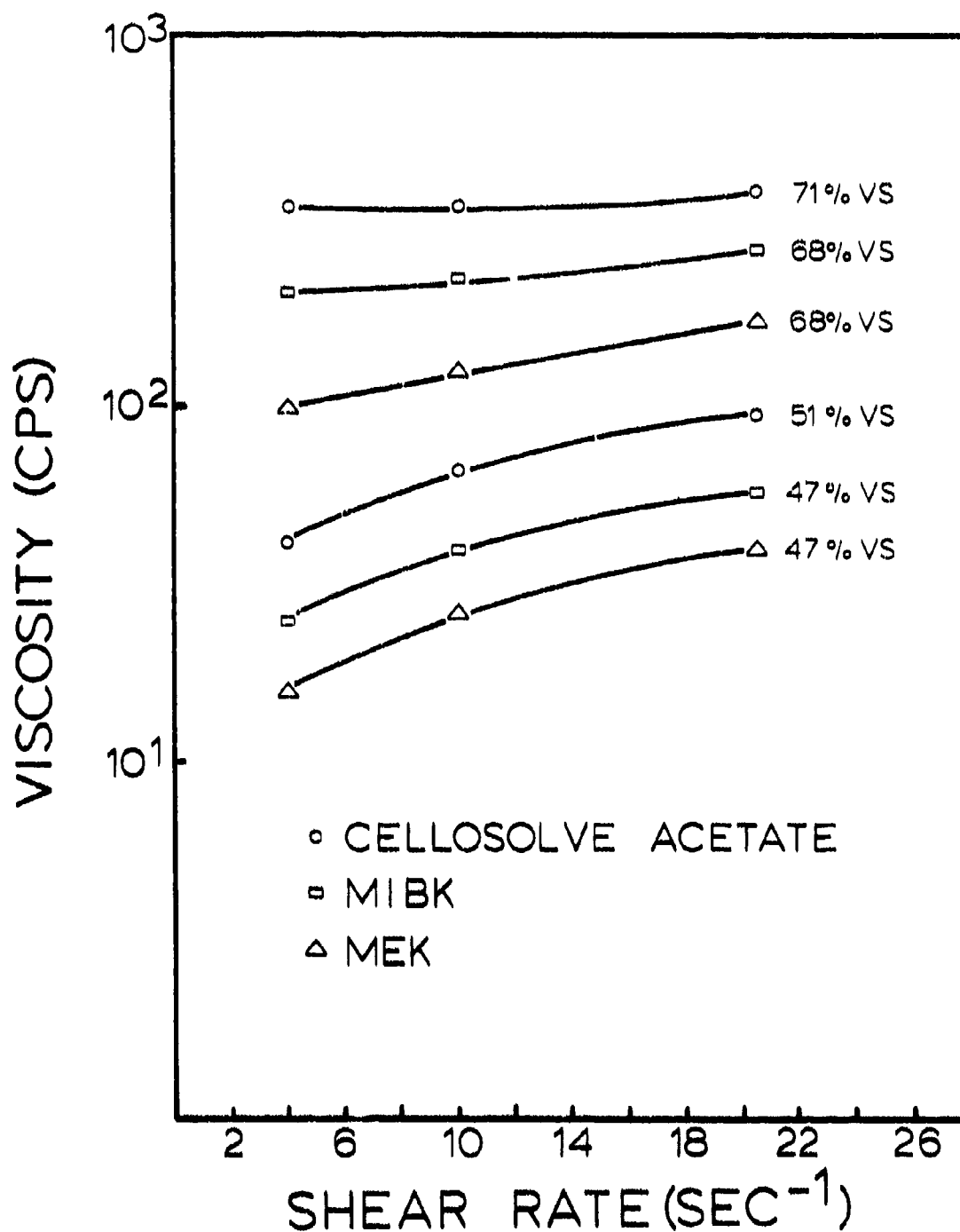


Figure 8. Cargill 5760 Rheogram
Brookfield Synchro-Lectric
#2 Spindle 298°K (77°F)

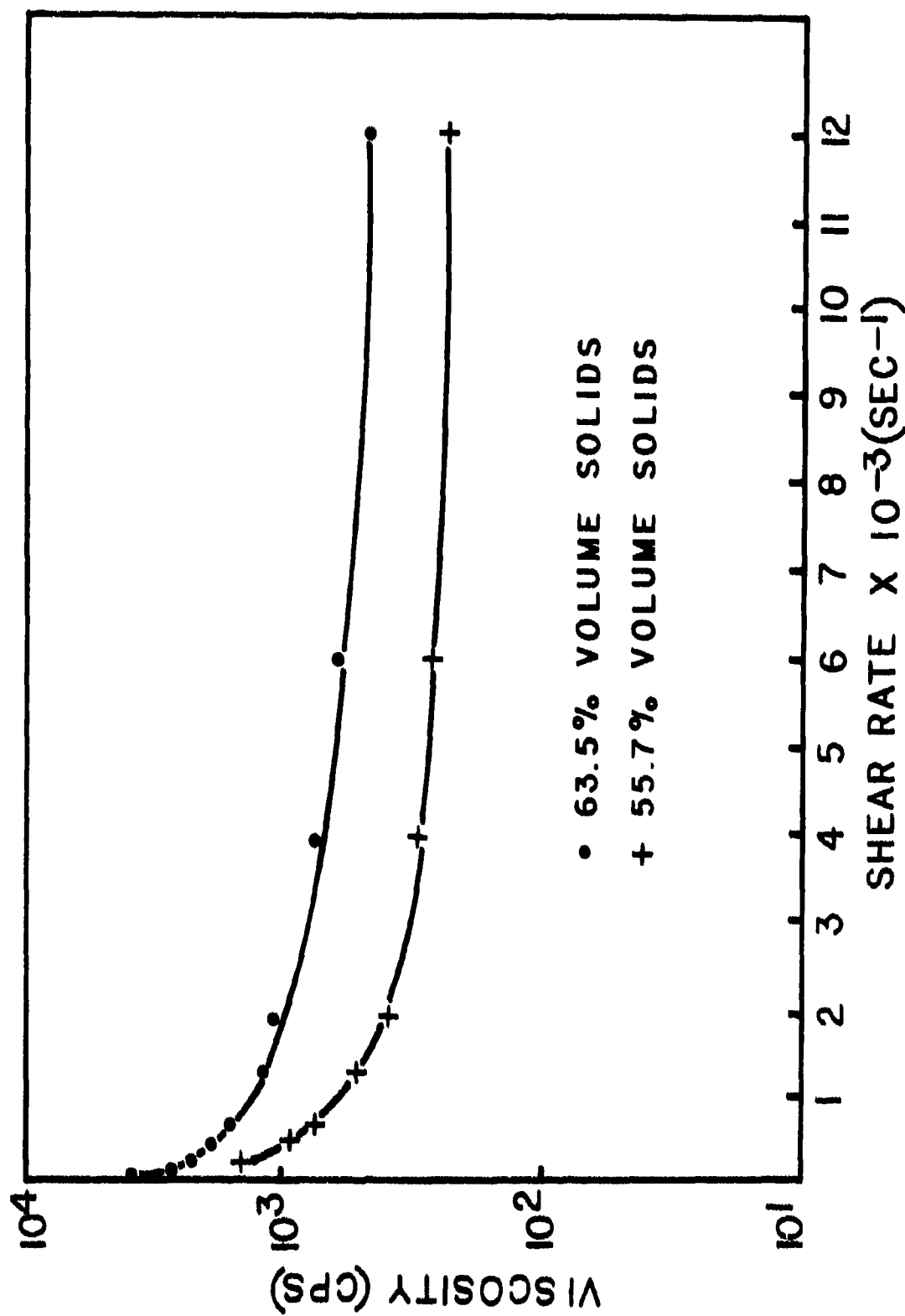


Figure 9. Multirion R-221-75 Rheogram

Haake Rotovisco

292 $^{\circ}$ K (67 $^{\circ}$ F)

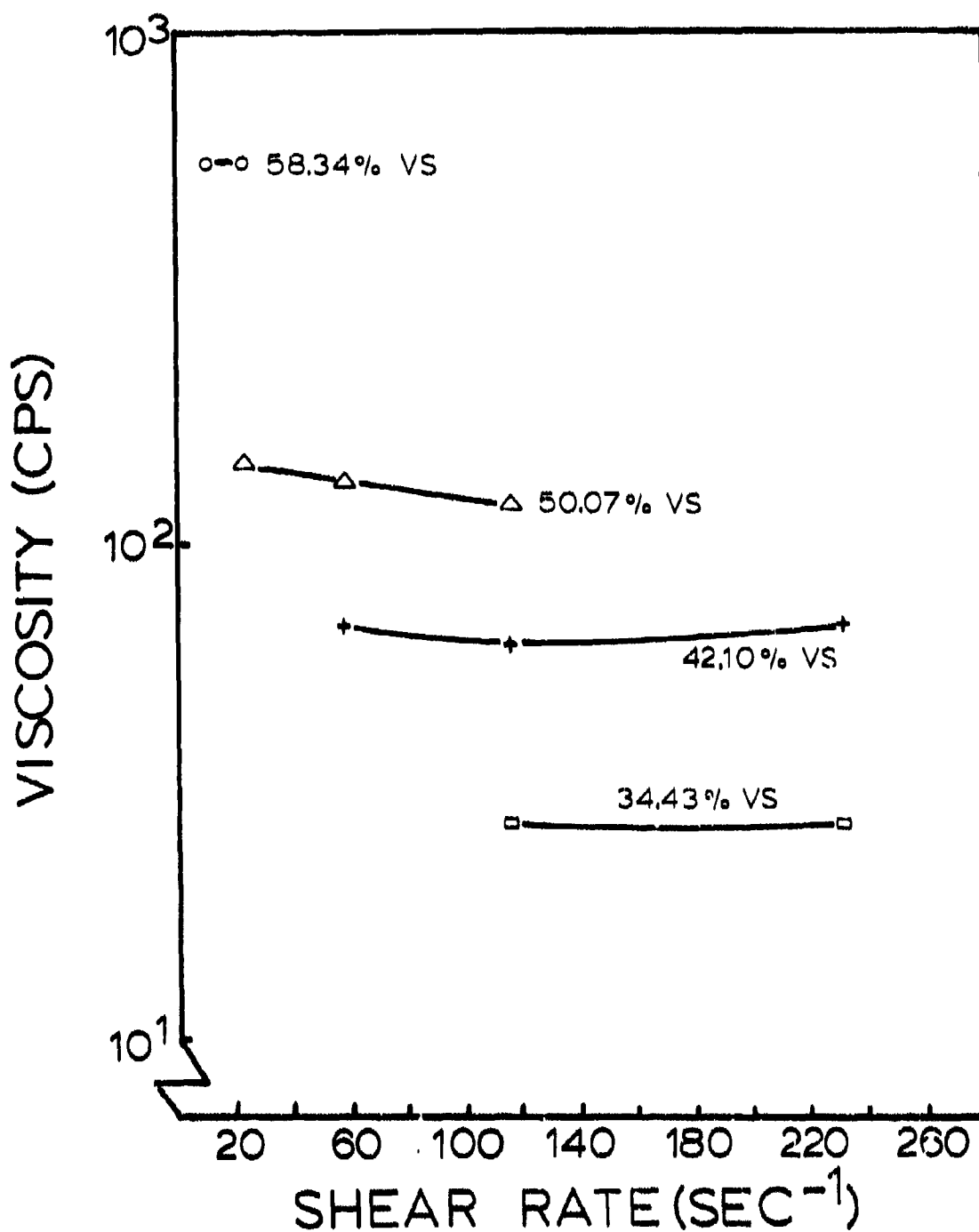


Figure 10a. Aroplaz 6025-A1-80/Cellosolve Acetate Rheogram
Wells-Brookfield 298°K (77°F)

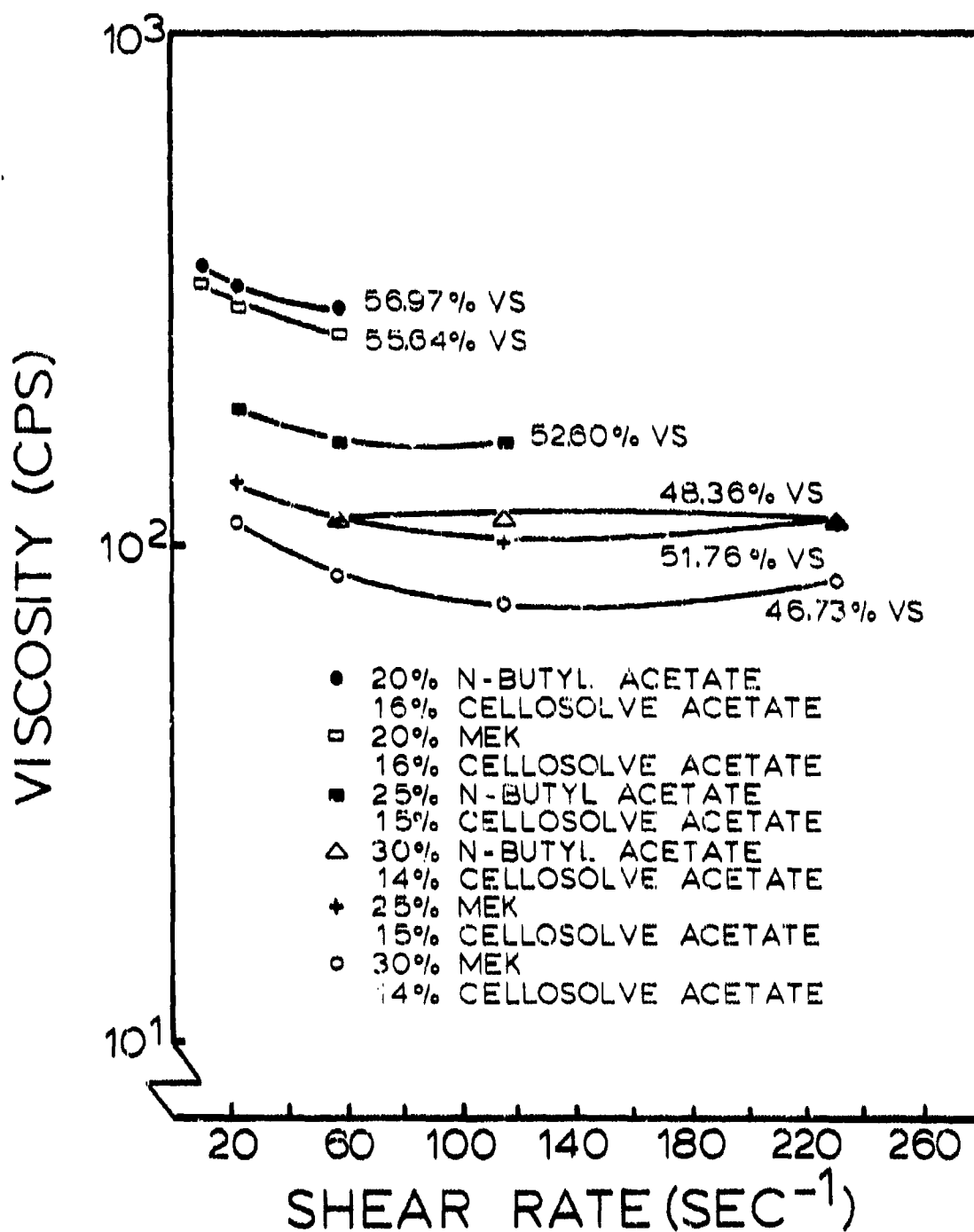


Figure 10b. Aroplaz 6025-A1-80/Solvent Blends Rheogram
 Wells-Brookfield 298°K (77°F)

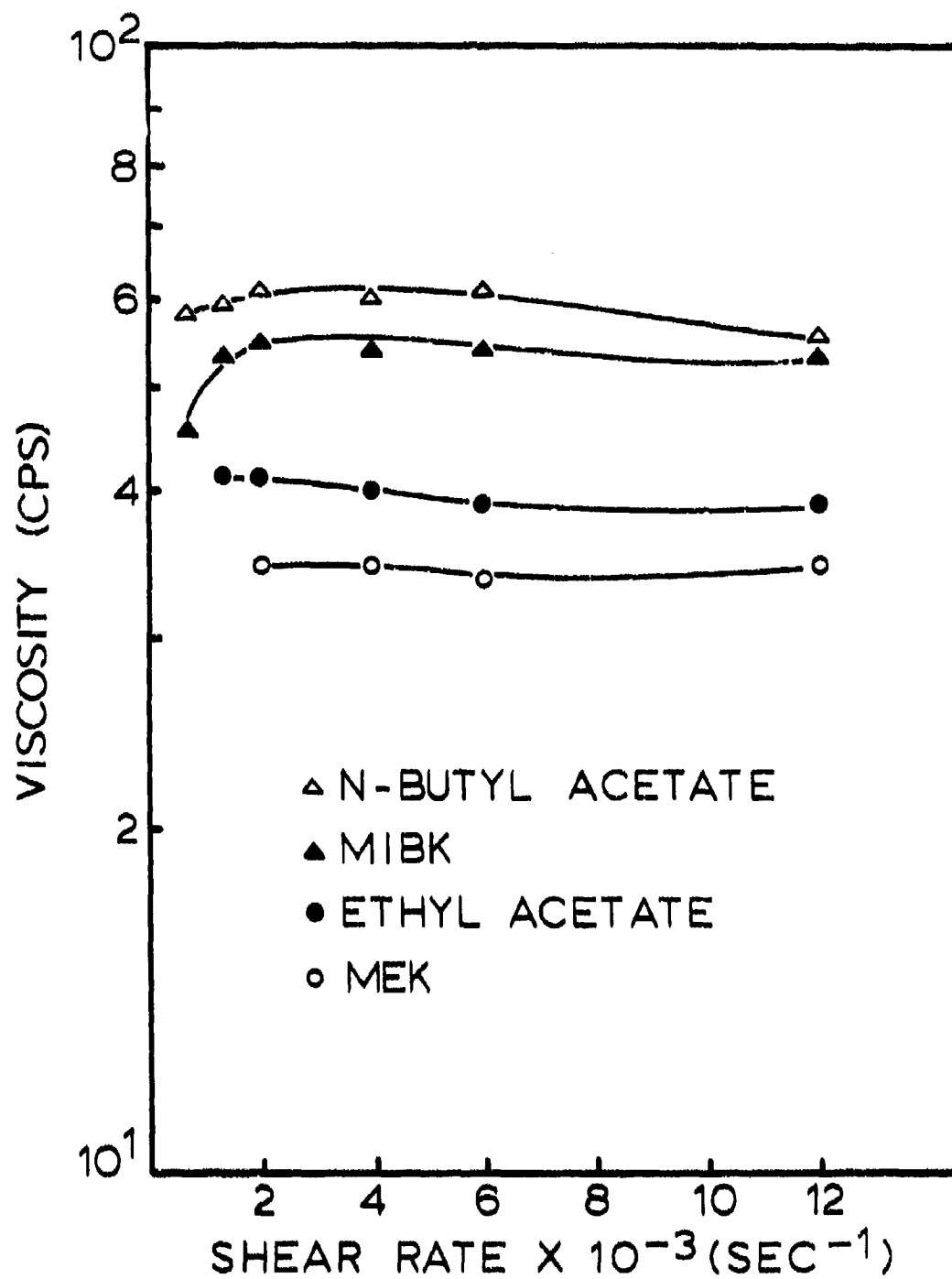


Figure 11. NIAX PCP-0300 Rheogram

Haake Rotovisco

296°K (73°F)

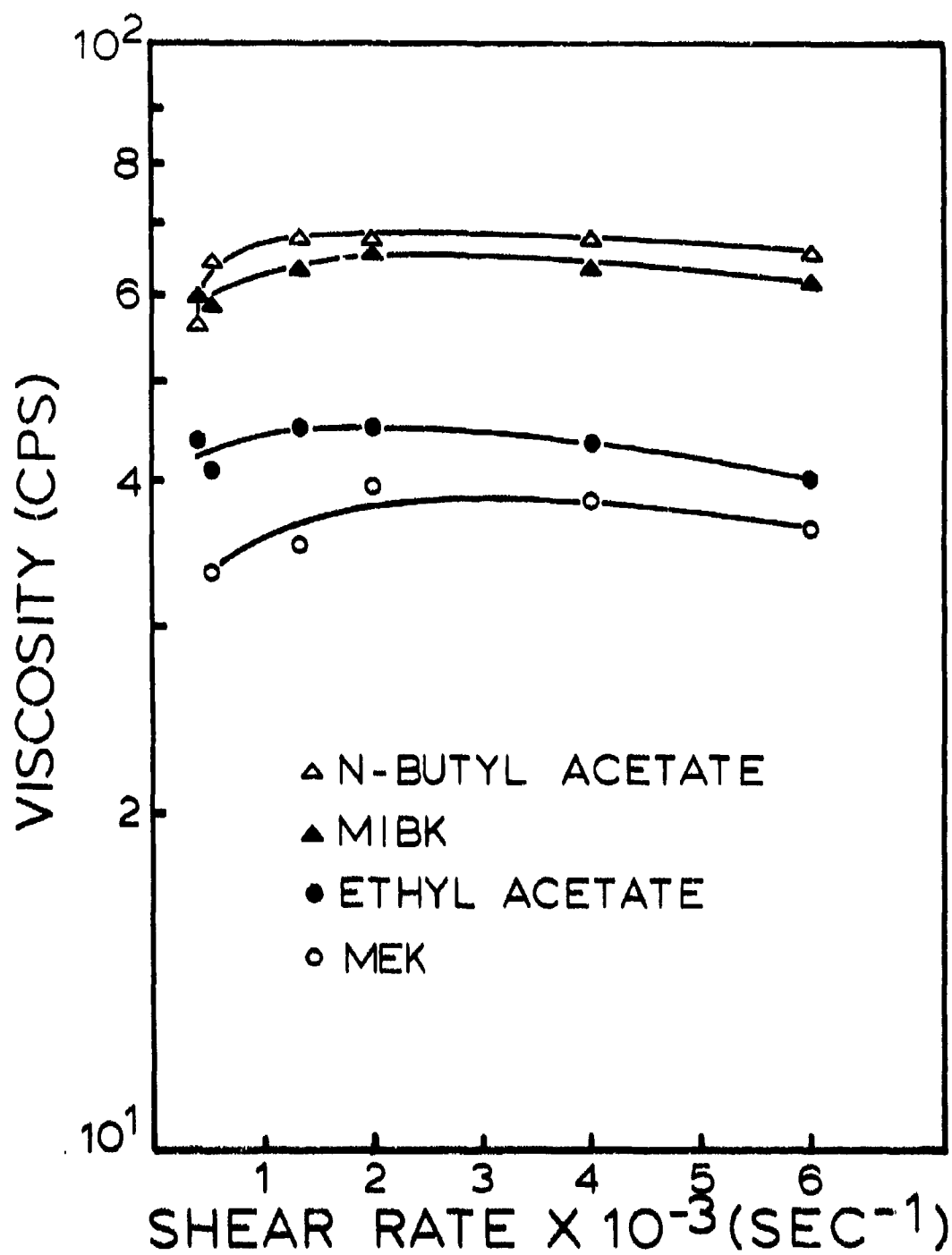


Figure 12. NIAX PCP-0310 Rheogram

Haake Rotovisco
296°K (73°F)

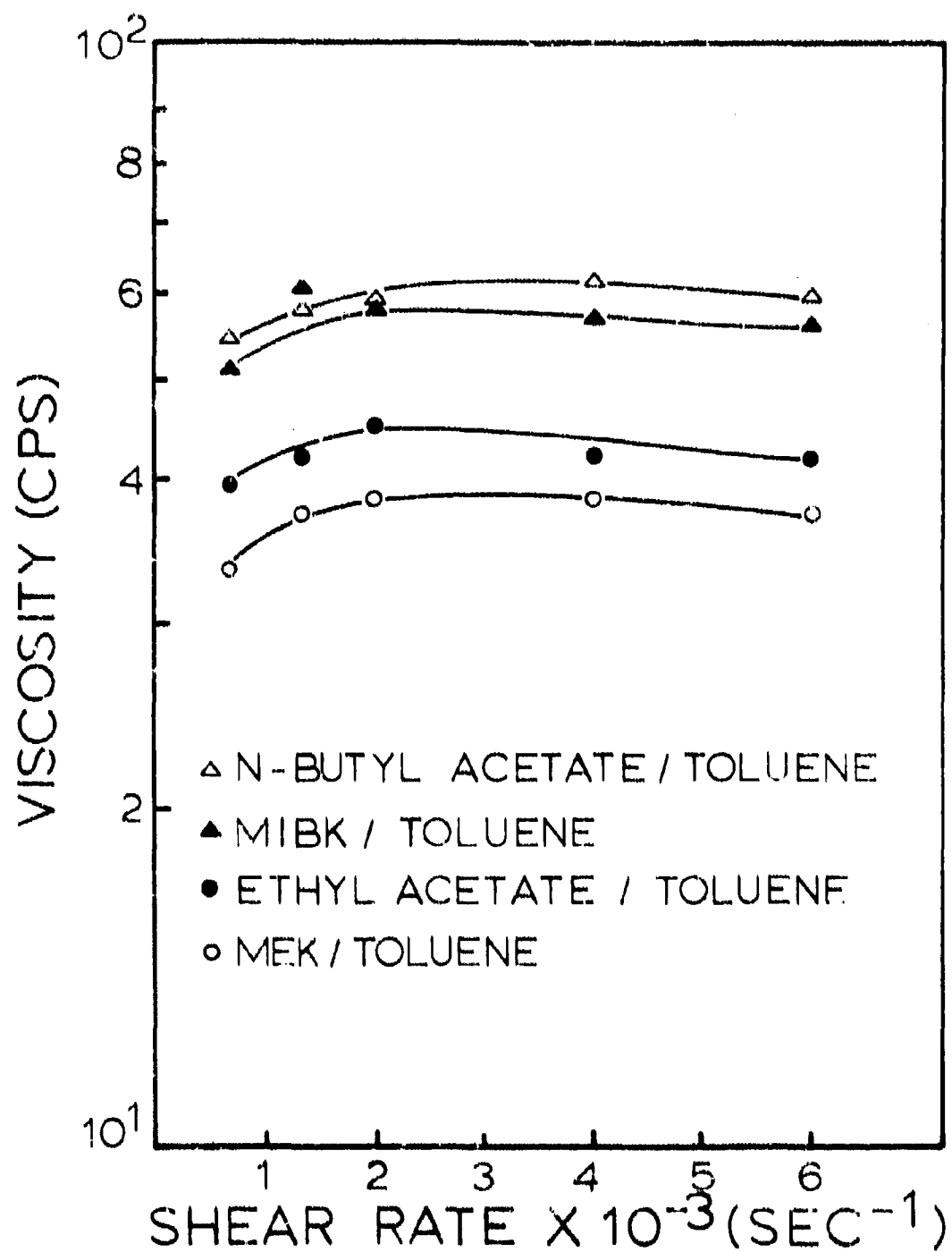


Figure 13. NIAX PCP-0210 Rheogram

Haake Rotovisco

296⁰K (73⁰F)

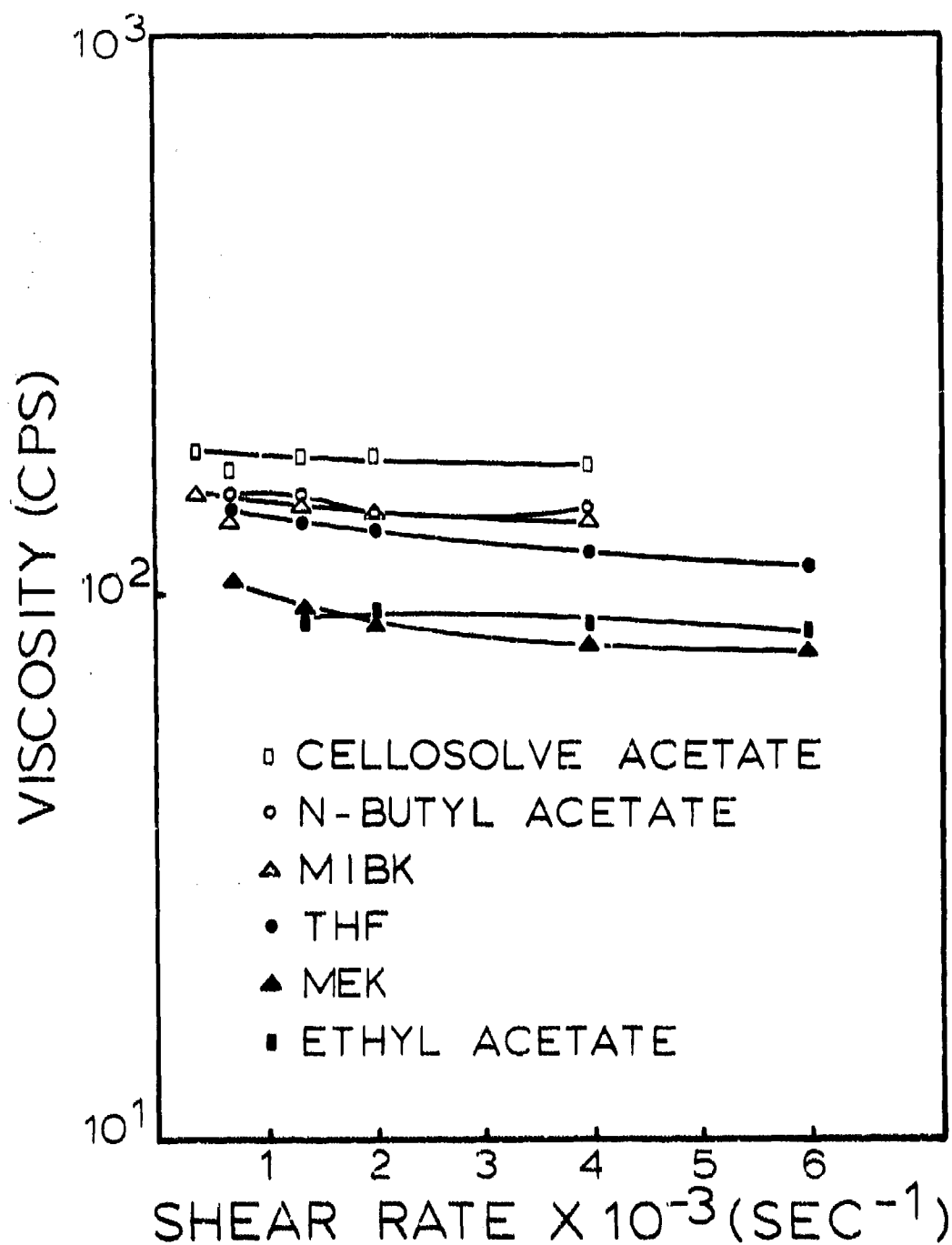


Figure 14. Pluracol PCP-450 Rheogram

Haake Rotovisco

298°K (77°F)

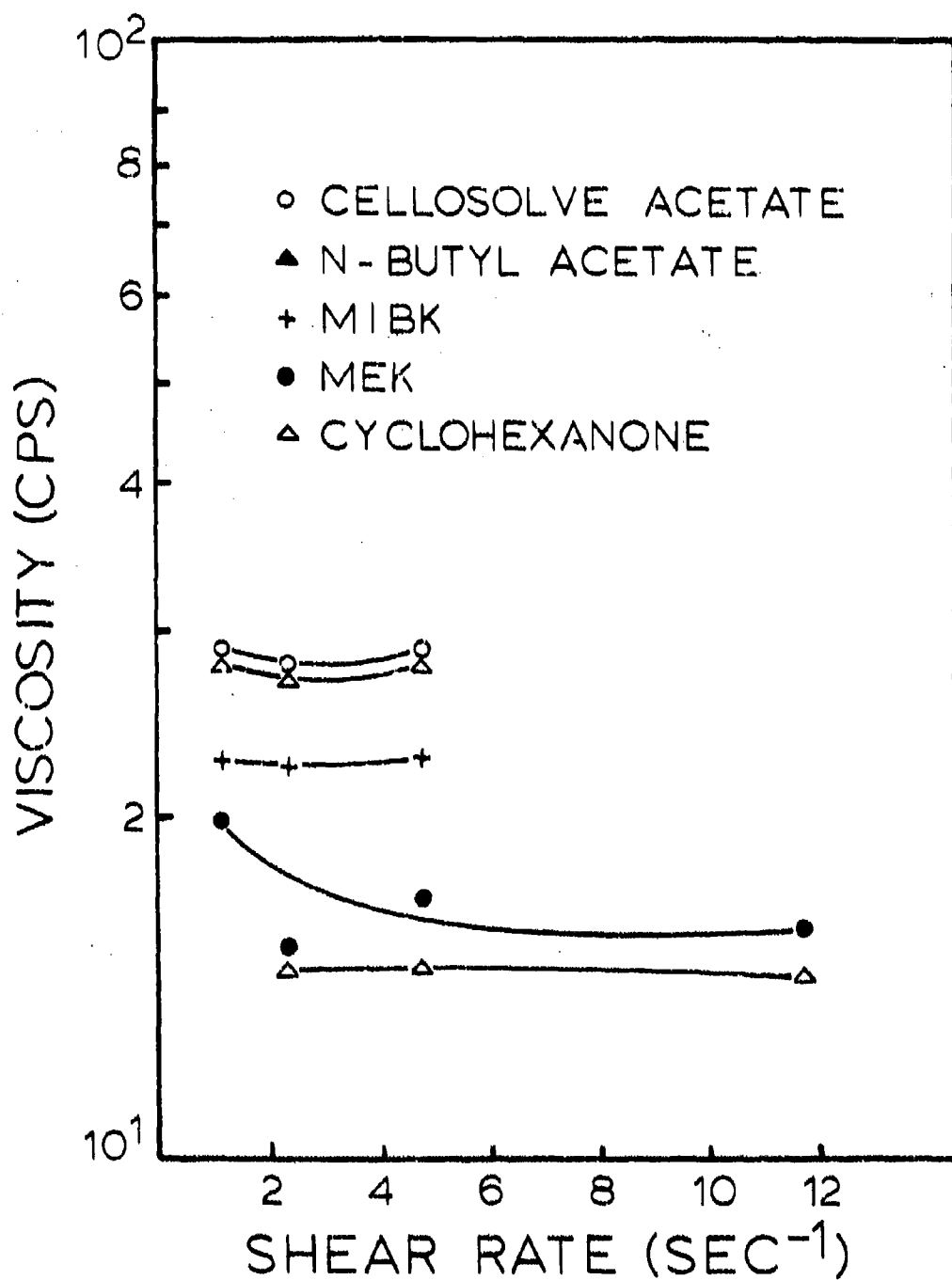


Figure 15. Desmodur N-100 Rheogram
Wells-Brookfield
298°K (77°K)

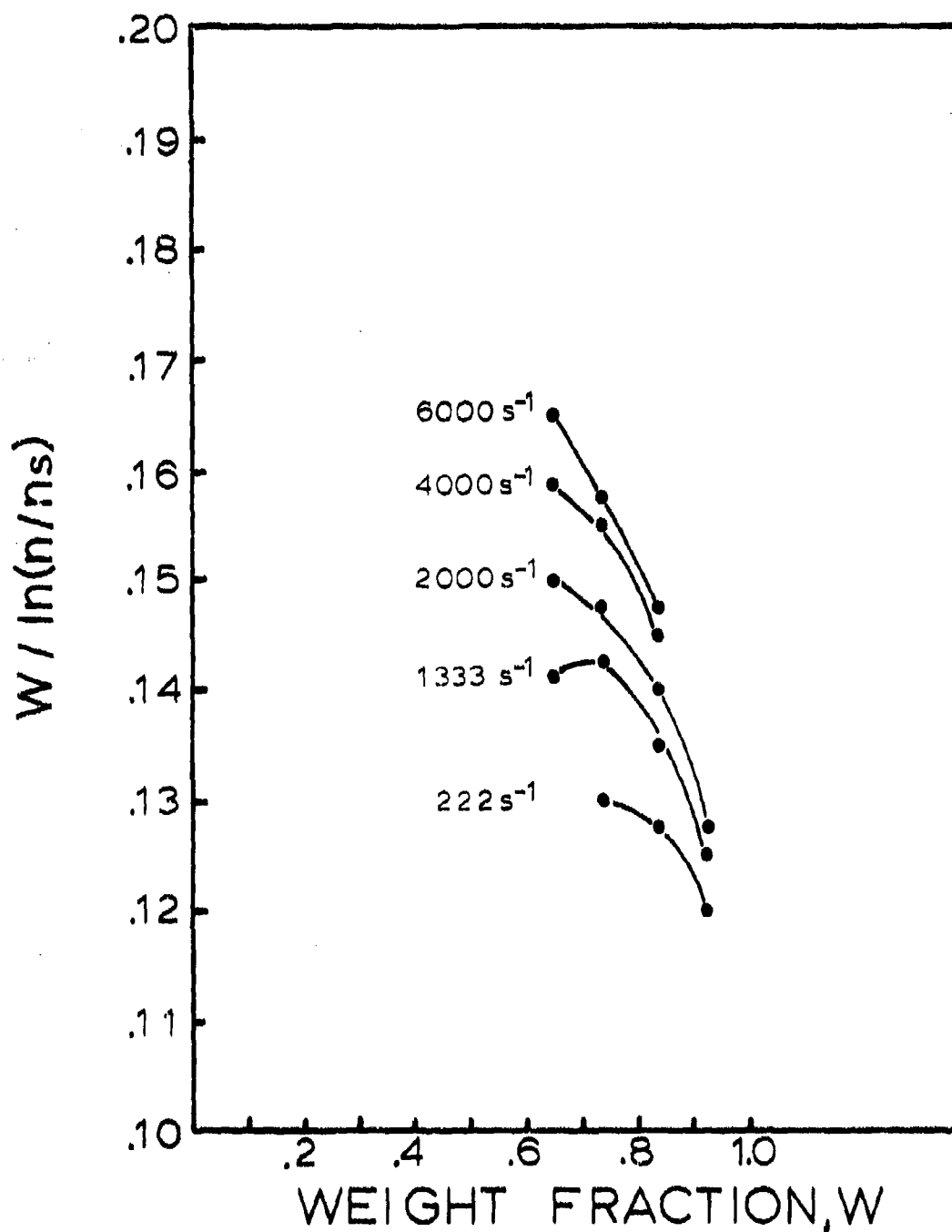


Figure 16. Acryloid AU-568/Cellosolve Acetate Erickson Plot
Haake Rotovisco 292°K (67°F)

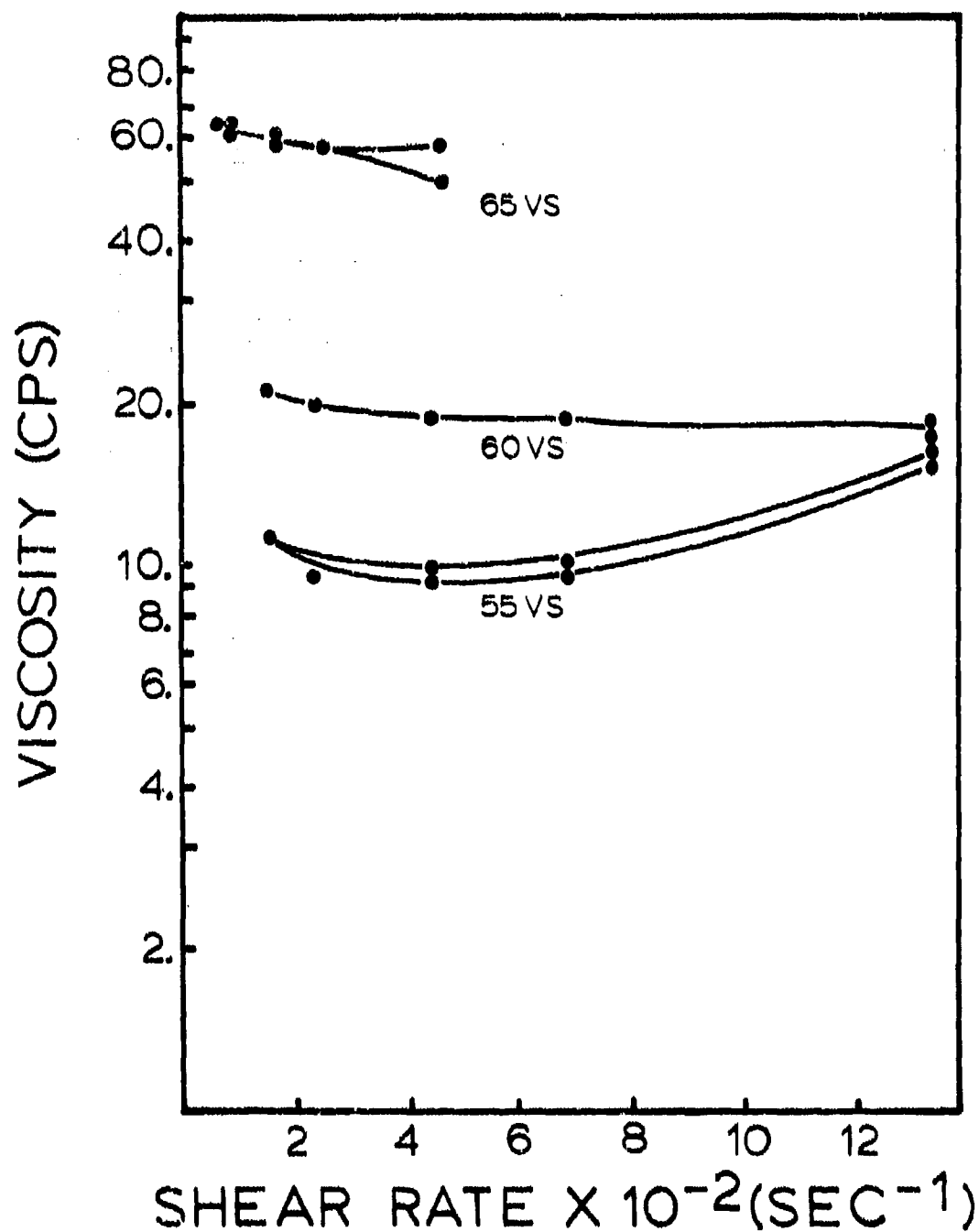


Figure 17. Acryloid AU-568/TiO₂ Dispersion
Viscosity-Shear Rate Profiles
Haake Rotovisco 298°K (77°F)

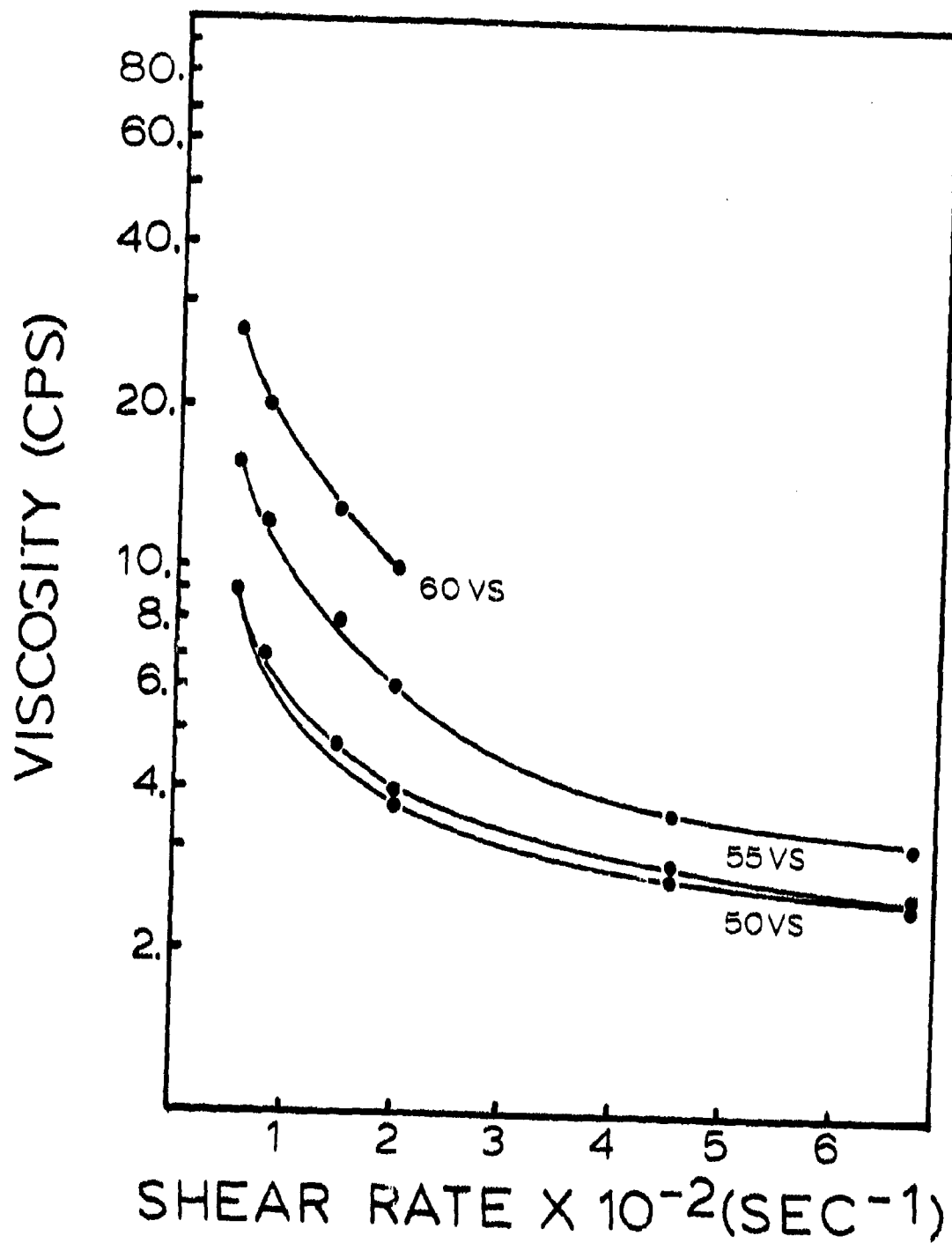


Figure 18. Cargill 5760/TiO₂ Dispersion
Viscosity Shear Rate Profile
Haake Rotovisco 298°K (77°F)

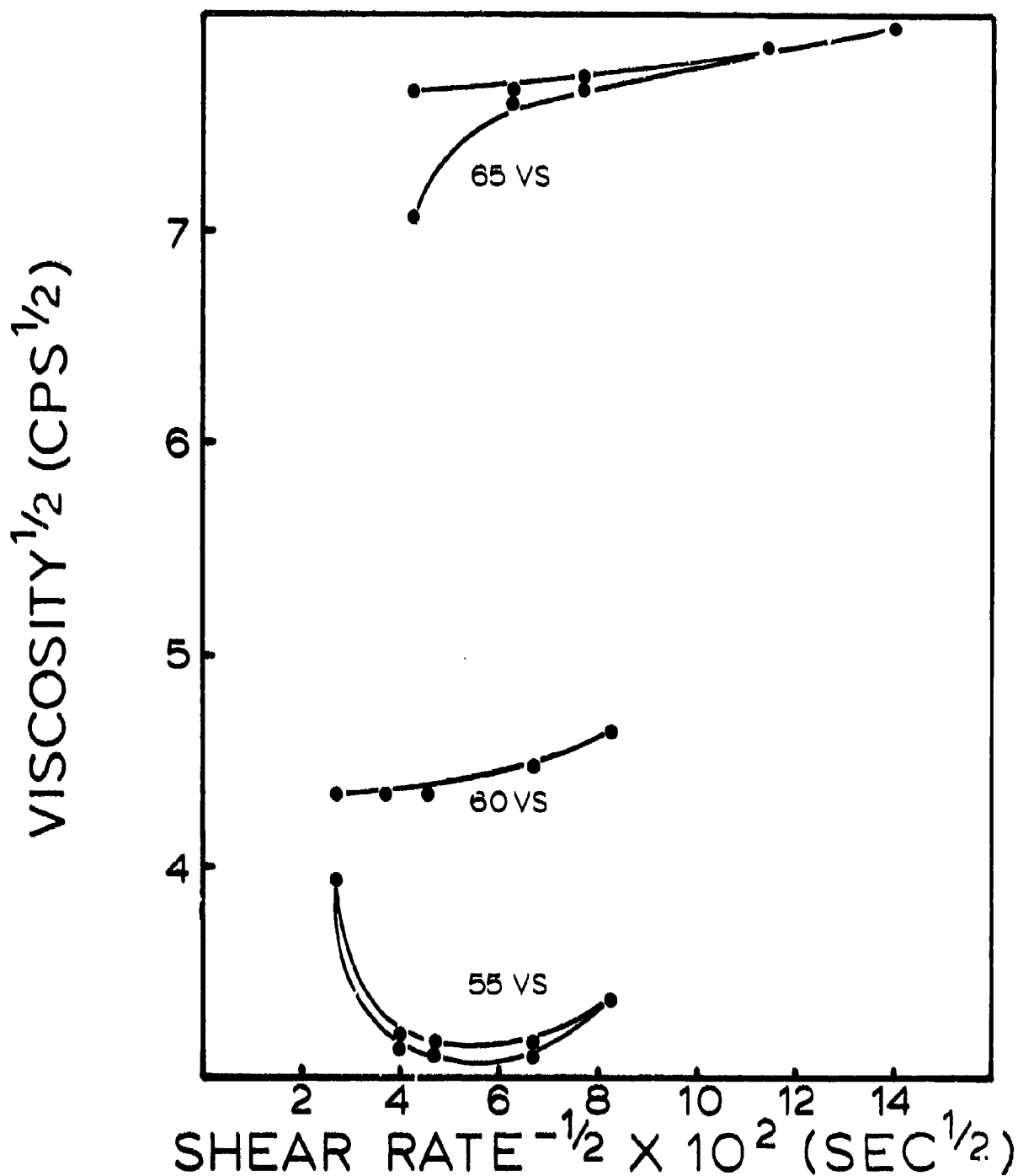


Figure 19. Acryloid AU-568/TiO₂ Dispersion Casson Plot

Haake Rotovisco 298°K (77°F)

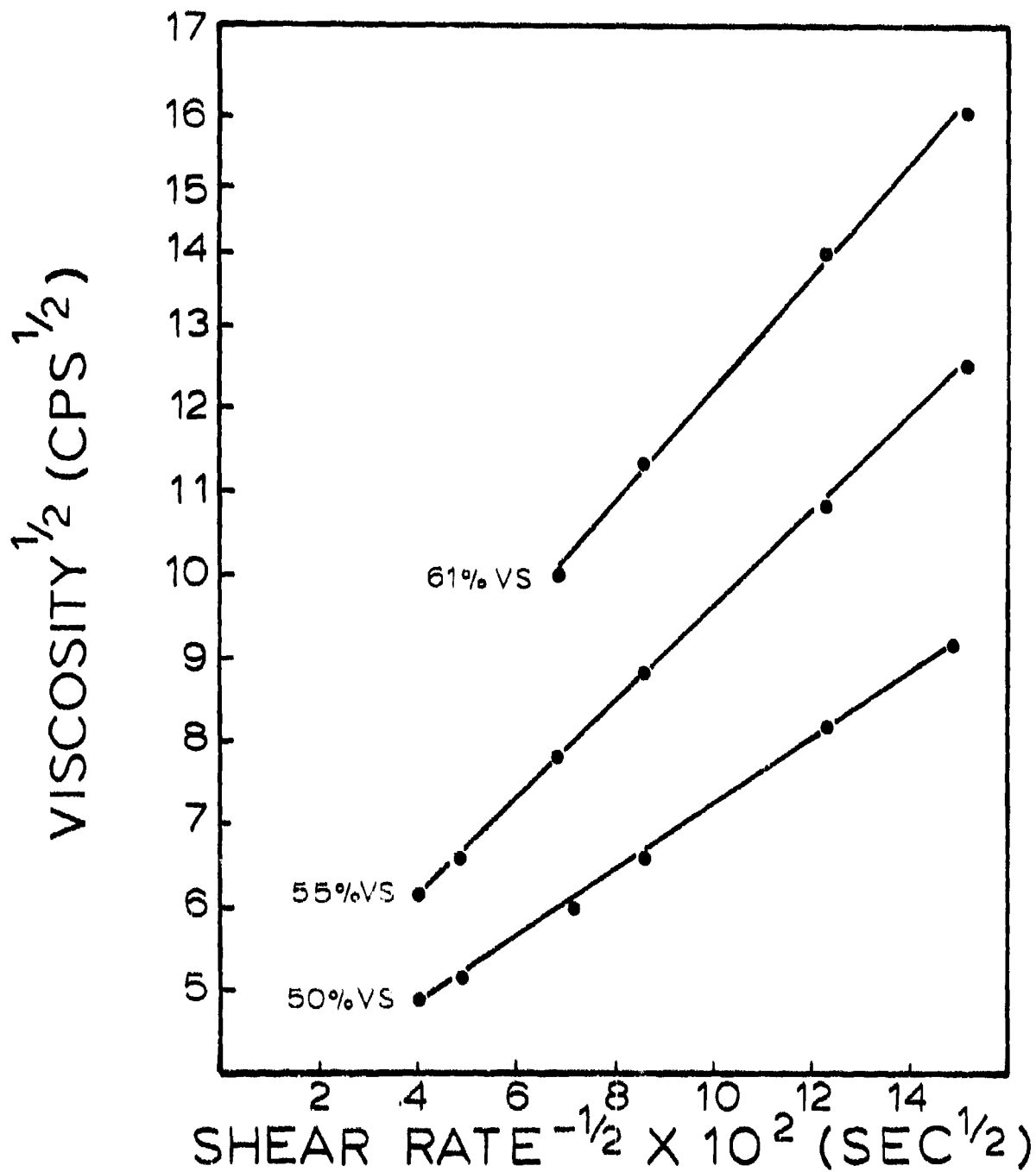


Figure 20. Cargill 6760/TiO₂ Dispersions Casson Plot
Haake Rotovisco 298°K (77°F)

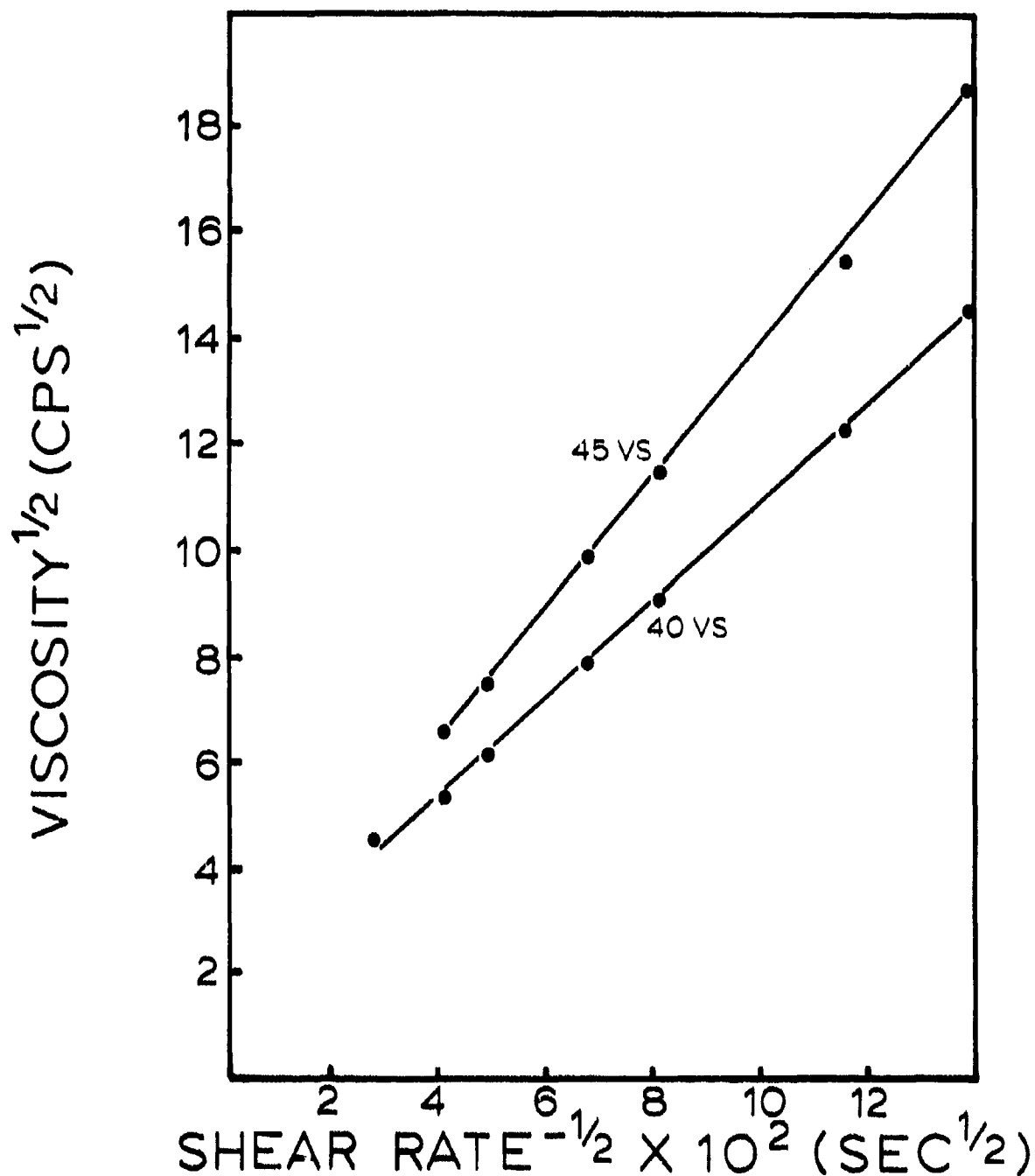


Figure 21. NIAx PCP-0300/TiO₂ Dispersions Casson Plot

Haake Rotovisco 298°K (77°F)

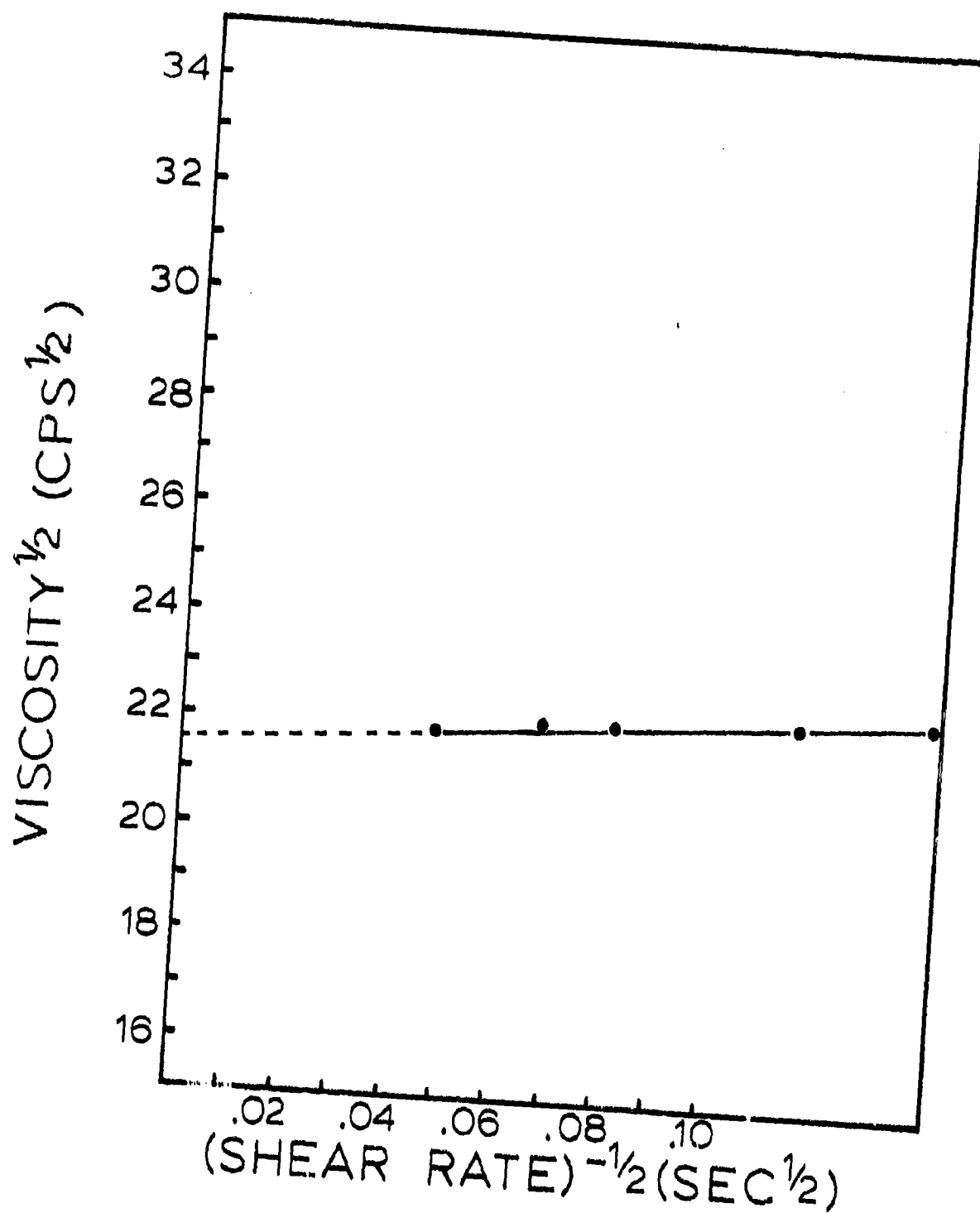


Figure 22. White Pigmented Base 821X330 Casson Plot
Haake Rotovisco 296°K (73°F)

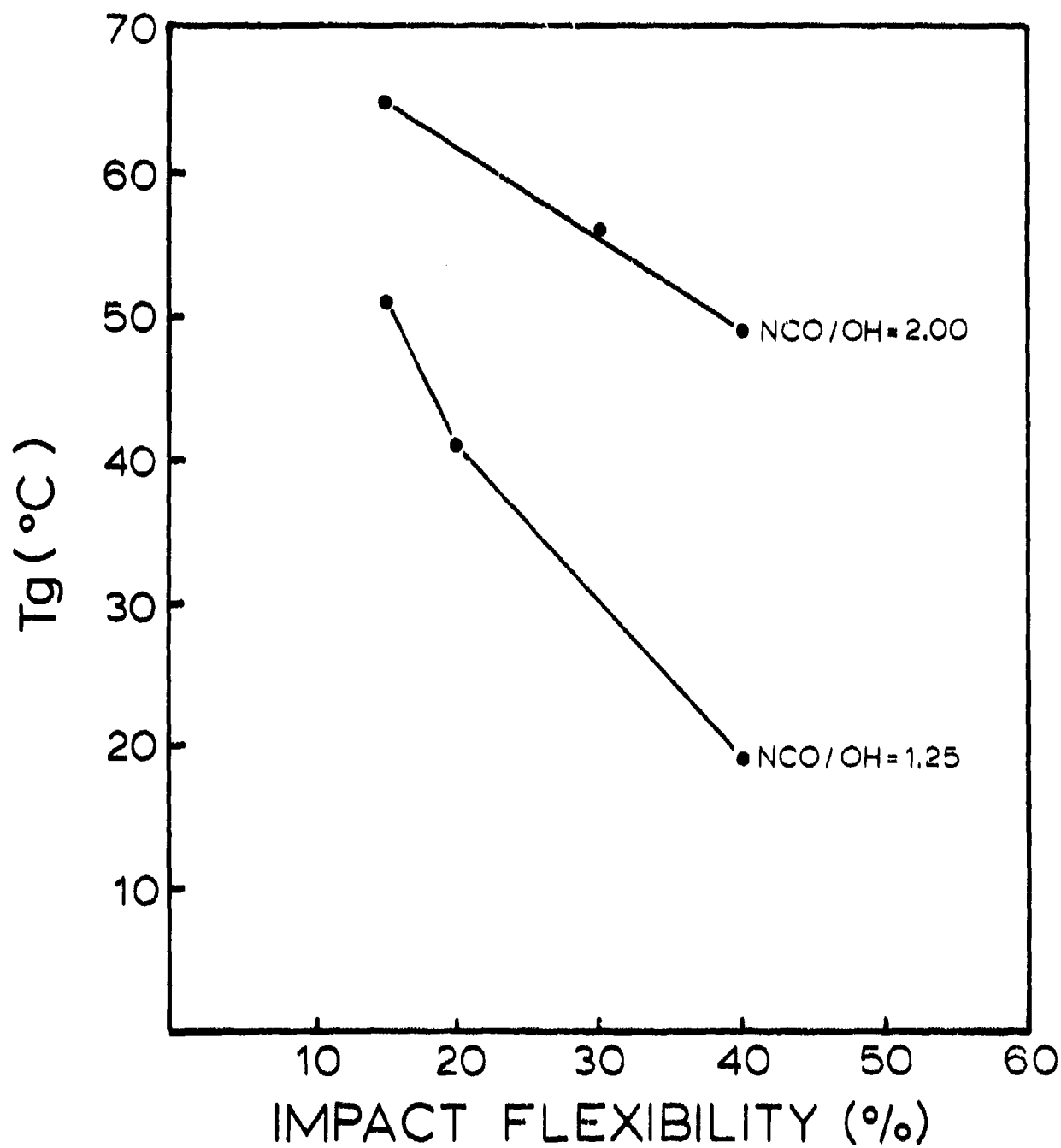


Figure 23. T_g vs Impact Flexibility Acryloid AU-568/NIAX
PCP-0300/Desmodur N-100 Systems at 10 Percent PVC

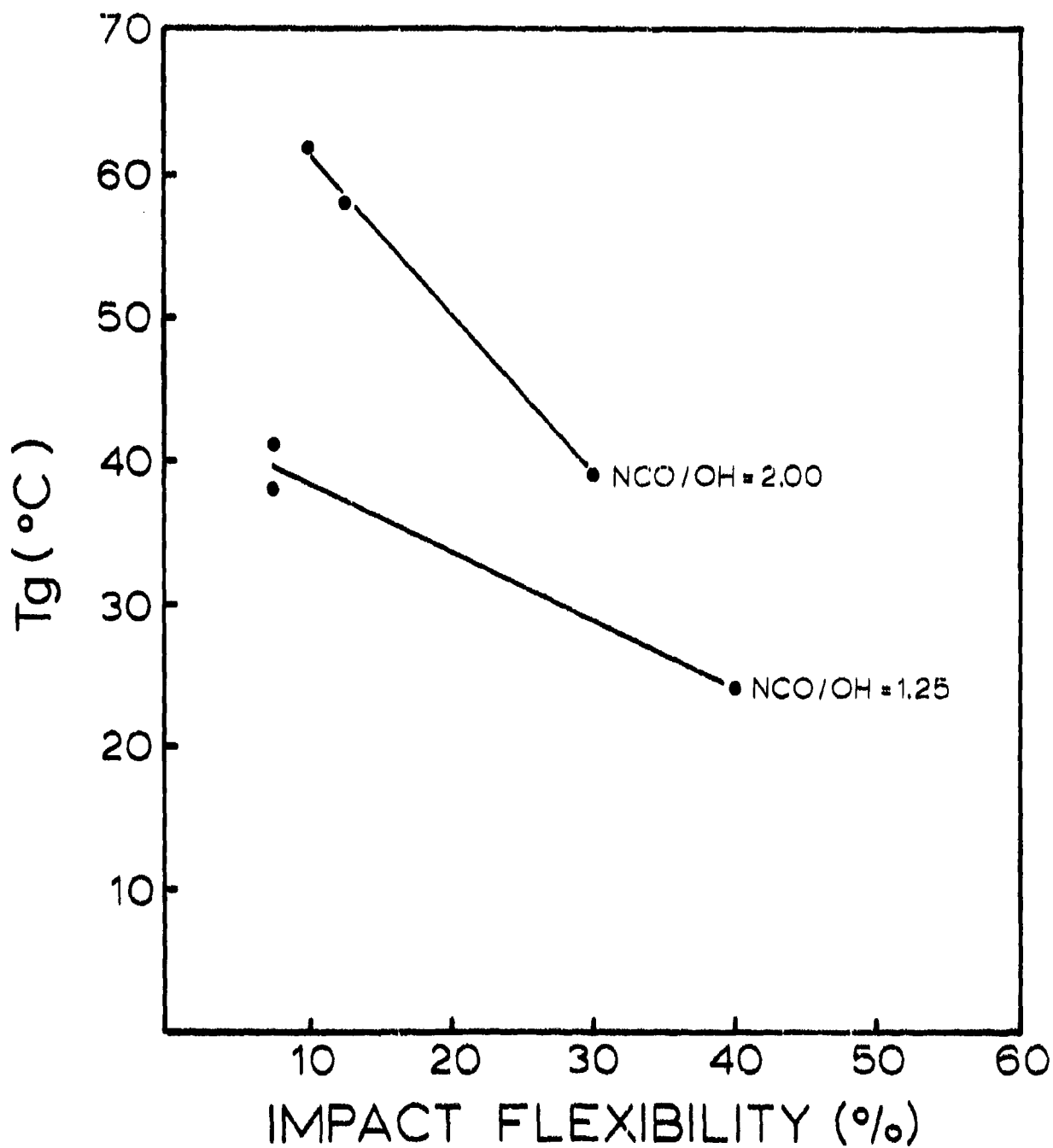


Figure 24. T_g vs Impact Flexibility Acryloid AU-568/NIAX
PCP-0300/Desmodur N-100 Systems at 18 Percent PVC

APPENDIX A

HIGH SOLIDS COATING SYSTEM - EXPANDED CONTRACT
TO CONSIDER TRANSFER OF DEVELOPED TECHNOLOGY
TO THE TRANSPORTATION AND APPLIANCE INDUSTRIES

Executive Summary

1.0 Introduction

This summary is the result of an investigation of the feasibility of transferring high solids coatings technology developed under support of the Air Force Materials Laboratory (Contract No. F33615-77-C-5101) to the needs of the transportation and appliance industries. The funding for the feasibility study was provided by the Environmental Protection Agency via the AFML (WPAFB).

The goal of the Air Force program was the development of a 65% volume solids, sprayable (airless electrostatic method), high performance polyurethane coating for exterior aircraft application. Environmental concern indicating further reduction or elimination of solvents from coatings was a major consideration. Ancillary benefits that may accrue include: reduced application costs due to the increased level of coatings applied at each spray pass, cost savings due to reduced solvent costs, and savings due to reduced freight, handling, and storage costs. Additionally, employment of ambient cure systems will produce energy savings.

Transfer of high solids coatings technology developed for aerospace applications to other industries cannot be assumed to be direct. The aerospace industry generally utilizes chromate pretreated and primed aluminum as the substrate and has its own unique performance requirements.

The transportation industry employs a steel substrate pre-treated with a zinc phosphate system. The substrate is primed with either a red oxide based spray primer or a black anodically electrocoated primer. The transportation industry's performance standards are also unique.

The results of this feasibility study indicate that the technology under development for the aerospace industry provides a good basis for development of high solids coatings for use in the transportation and appliance industries. The major problems lie in application technology and further refinement of the performance characteristics.

2.0 Discussion

The performance and applications properties of a coating are, in part, a function of the substrate being coated. Coatings are designed to fulfill two basic functions: protection and decoration. The protection function requires that the coating be durable under the anticipated use conditions, i.e., resistant to moisture, corrosive or degradative substances, sunlight, etc. In addition, the coating will be required to resist mechanical damage such as abrasion and impact. The outer coating matrix must be chemically and mechanically durable. However, the outer coating cannot effectively perform its task if the substrate does not permit adherence and, in many cases, add to the protective qualities of the overall

coating system. Primers and pretreatments are then required in these cases.

The outer coating designed for adherence to and protection of an aluminum surface which has been pretreated and primed with materials containing chromates may not readily adhere to a phosphate pretreated, red oxide primed steel surface. The transfer of a coating system specifically designed for one substrate to another substrate may be difficult, if not impossible, without considerable modification.

While this discussion has been general, the point that a coating or "paint" is not an entity in itself, but it is almost always a part of a protective, decorative system must not be overlooked.

The prognosis derived from this preliminary study is positive. The concepts developed in the high solids program for Aerospace applications have been demonstrated to be sound and transferable.

3.0 Experimental Summary

The experimental approach chosen for the high solids aerospace program was the evaluation of the viscosity concentration profiles of the components to be blended into high solids formulations. From this data, the solvents and prepolymers exhibiting viscosities best suited for the selected method of application were determined.

The selected solvents and prepolymers were formulated into two-component systems ("polyol" and isocyanate) and spray applied (50 psi) to primed and pre-treated aluminum substrates. After curing for seven days at constant temperature and humidity, the resulting films were evaluated for physical, chemical, and durability properties as specified by MIL-C-83286. (Table I)

The best "polyol" prepolymers from the aerospace programs, oxazolidines and polyols, were evaluated for incorporation into high solids formulations for application over steel. Acryloid AU-568, an oxazolidine based prepolymer from Rohm and Haas, when reacted with moisture, converts to an alkanolamine. When blended with Desmodur N-100 (an isocyanate from Mobay Chemicals) the alcohol and amine functionalities react to produce urethane and urea linkages. The resulting films exhibit good fluid resistance but poor flexibility. NIAX PCP-0300, a polycaprolactone, from Union Carbide when crosslinked with Desmodur N-100, produced films with good flexibility but poor fluid resistance. Each of the above and following formulations were pigmented with TiO_2 .

To optimize the performance properties of these simple systems a formulation study was undertaken. This involved preparation of various blends of Acryloid AU-568 with NIAX PCP-0300 to produce the "polyol" component of

the topcoat formulation. These mixtures were blended with Desmodur N-100. The isocyanate levels (NCO/OH) and pigment volume concentrations (PVC) were varied. In addition, the levels of the two components within the polyol blend were varied. These candidate formulations were evaluated for application over steel and aluminum substrates. Systems evaluated previously for performance over aluminum in the Aerospace program and which exhibited the requisite physical properties were also evaluated for application over steel substrates.

The substrates used in this program were cold rolled steel test panels treated with Bonderite 40, a proprietary zinc phosphate from the Parker Division of OXY Metal Industries Corporation. The test substrates were primed respectively, with two primers developed by De-Soto for general industrial use. One primer was a gray anodic electrocoat primer which possesses good salt spray and detergent solution (Lactrogar) resistance. The other, a spray applied primer, was a chromate pigmented material (Koropon Low Bake Primer 561 X 301). Both primers require baking for proper cure.

The performance specifications developed for use by the transportation industry are based on past experience. For this investigation, the Fruehauf Engineering Standards (Fruehauf Engineering of Detroit, manufacturers of trucks

and truck parts) were designated as the performance specifications. (Table I) The test panels were evaluated for salt spray resistance (ASTM B-117-64), weatherometer resistance (ASTM E 42-57), film flexibility (ASTM D 522-60), and water resistance (ASTM D-870-44).

The compositions of the three formulations which exhibited the best performance properties over steel attained within this program are listed in Table II. Of these formulations, 2408-9 is the formulation which most closely approximates the program goals when applied by air spray techniques. (See Table III). This formulation exhibits superior performances for salt spray resistance, accelerated weathering, and reverse impact. The performance properties of the coatings applied over the Koropon spray primer are better than those of the coatings applied over the electrocoat primer.

Another objective of the program was the development of a high solids coating suitable for application by airless electrostatic spray. Because the primary interest of the expanded contract was the determination of the performance properties over steel substrates, only preliminary studies on this application technique were made. When applied by this technique, the "best" formulation (2408-9) exhibits acceptable atomization. However, some fingering (streams of unatomized material) appears

at the top and bottom of the spray fan. Considerable foaming and sagging is noted in the films. Effort to perfect this application technique is being continued.

The best prototype formulation (2408-9) in its present state exhibits properties which could create handling difficulties during in-field use. The pot life of the formulation is less than one hour. During this time interval the viscosity continually increases, atomization during spraying becomes coarse, and the applied coating does not exhibit good leveling properties. Two approaches which may be taken to correct this problem exist. The catalyst and/or the catalyst concentration may be altered, or mix-in-head spray gun equipment may be used for application.

The spray characteristics (atomization, leveling, and amount of paint solids deposited) of high solids formulations are different from those with which the transportation and appliance industry is familiar. Plant personnel would need to be trained to control the critical deposition parameters in order to obtain high quality, reproducible coatings.

Test panels primed with spray or anodic electrocoat primers which are representative of those used by the transportation industry were received from Mack Truck. These panels and panels primed with DeSoto materials will

be topcoated with the best formulation developed.

The coated panels will be submitted to the Air Force
Materials Laboratory for their testing and evaluation.

TABLE I

Comparison of Typical Performance Specifications

MIL-C-83286

FRUEHAUF ENGINEERING

5% Salt Spray	No blistering, cracking, corrosion, or loss of adhesion after 500 hours of exposure.	No blistering, cracking, corrosion, or loss of adhesion after 500 hours of exposure.
100% Relative Humidity	No blistering, cracking, softening, or loss of adhesion after 720 hours of exposure.	Not applicable.
Accelerated Weathering	After 500 hour exposure the coating should exhibit 60% impact flexibility, no more than 10% loss of original gloss, and no color change.	No color change, chalking, checking, or other film defects after 250 hours of exposure.
Fluid Resistance	A decrease of no more than one pencil hardness unit after immersion in water (4 days, 100°F), lubricating oil (24 hours, 250°F), hydrocarbon fluid (7 days, room temperature), and hydraulic fluid (7 days, room temperature). A decrease of no more than two pencil hardness units after immersion in Skydrol 500B fluid (7 days, room temperature).	No cracking, blistering, or checking after 100 hours in distilled water at 100°F.
Film Flexibility	No cracking, crazing, or loss of adhesion of coating when elongated 60% by impacting mandrel.	No cracking or loss of adhesion when deformed 180° over conical mandrel (maximum elongation - 26%).
Low Temperature Flexibility	No cracking or loss of adhesion when bent around 3/8 in (9.5 mm) diameter cylindrical mandrel after four hours at -65°F (-54°C). (Test immediately after removal from cold box).	Not applicable.
High Temperature Resistance	No loss of adhesion or flexibility after four hours at 300°F (149°C).	Not applicable.
Reverse Impact	Not applicable.	>80 in-lbs.
50° Gloss	>90	>90

TABLE II

Prototype High Solids Formulations

Formulation Code	Component	Material	Weight Percent (%)	Volume Percent (%)
2347-34	Pigment	TiO ₂	21.39	6.42
	Oxazolidine	Acryloid AU-568	26.08	28.58
	Diisocyanate	DDI 1410	7.96	10.10
	Biuret polyiso- cyanate	Desmodur N-100	23.90	24.58
	Solvent	U.G. MEK	20.67	30.32
2347-40	Pigment	TiO ₂	34.05	11.70
	Oxazolidine	Acryloid AU-568	21.41	26.82
	Biuret polyiso- cyanate	Desmodur N-100	26.28	30.86
	Solvent	U.G. MEK	18.26	30.62
2408-9	Pigment	TiO ₂	20.93	6.40
	Oxazolidine	Acryloid AU-568	17.74	19.95
	Polycaprolactone	NIAX PCP-0300	5.91	6.47
	Biuret polyiso- cyanate	Desmodur N-100	34.05	35.63
	Solvent	U.G. MEK	20.79	31.00
	Catalyst	Dibutyl Tin dil- urate	0.58	0.55

TABLE III

Prototype Formulation Performance Properties

Based on Fruehauf Standards

Formulations									
2347-34					2408-9				
Primer					Primer				
Spray		Electro-coat		Spray		Electro-coat		Fruehauf Requirements	
Salt Spray Resistance	loss of adhesion along scribe lines	loss of adhesion along scribe lines	loss of adhesion at scribe intersection	loss of adhesion along scribe lines	loss of adhesion along scribe lines	loss of adhesion at scribe intersection	loss of adhesion along scribe lines (7)	2 mm loss of adhesion along scribe lines (7)	No blistering, cracking, or loss of adhesion after 500 hour exposure (numerical rating)
Accelerated Weatherings	43.1% Gloss Retention	87.8% Gloss Retention decrease in impact resistance from 20 to 5%	99% Gloss retention						No color change, chalking, checking, or other film defects after 250 hours exposure
Water Resistance	Blistered (1)	Pass (0)	Blistered (1)	Pass (0)	Pass (2)	Blistered (0)			No cracking, blistering, or checking after 100 hours immersion in water at 100°F (decrease in pencil hardness units)
Film Flexibility	Pass	Pass	Pass	Pass	Pass	Pass			No cracking or loss of adhesion when deformed 180° over a conical mandrel (26% maximum elongation)
Reverse Impact	40-78 in-lbs	22-30 in-lbs	36-54 in-lbs	4-20 in-lbs	73-80 in-lbs	38-48 in-lbs			>80 in-lbs.
60° Gloss	90.3	85.8	93.0						

Appendix B

Test Methods

1. Impact Flexibility

The flexibility was determined on 3 X 6 X 0.02 in (76 X 152 X 0.5 mm) 2024 T0 Alclad aluminum test panels, chromate pretreated and primed with MIL-P-23377. The G.E. impacting mandrel was dropped from a height of 24 inches. The elongated surfaces of the impacted coated panel were examined under 10X magnification for cracking and crazing of the coating. The impact flexibility requirements are 60% for gloss colors and 20% for camouflage colors. Adhesion of the coating to the elongated surfaces was evaluated by placing 250 masking tape (3M) to the surface, insuring adhesion and then removing with one abrupt pull. Any paint removal constitutes failure.

2. Heat Resistance

Test panels 3 X 6 X 0.020 in (76 X 152 X 0.5 mm) 2024 T0 Alclad aluminum, chromate pretreated and primed with MIL-P-23377, were exposed vertically to dry heat for 4 hours at 300°F (158.9°C). The panels were then tested for impact flexibility.

3. Low Temperature Flexibility

Test panels, 3 X 7 X 0.02 in (76 X 177 X 0.5 mm) 2024 T3 Alclad aluminum primed with MIL-P-23377, were for 4 hours at -63°F (-82°C). The panels, maintained at the specified temperatures, were then bent 180° over 3/8, 1/2, and 1 inch straight mandrels.

The panels were then examined for cracking or loss of adhesion.

4. Fluid Resistance

Test panels 2 X 4 X 0.02 in (51 X 102 X 0.5 mm) 2024 T3 Alclad aluminum, chromate pretreated and primed with MIL-P-23377, were tested for resistance to softening in the fluids listed below:

- a. Lubricating Oil: (Diester lubricating oil composed of 98 percent diisooctyl, and 2 percent tricresyl phosphate). Failure is indicated by a loss of greater than one pencil hardness unit after 24 hour immersion at $250 \pm 4^{\circ}\text{F}$ ($121 \pm 2^{\circ}\text{C}$).
- b. Hydrocarbon Resistance: (Type III fluid of TT-S-735) Failure is indicated by a loss of greater than one pencil hardness unit after 7 day immersion at room temperature.
- c. Hydraulic Fluid Resistance: (Hydraulic fluid of MIL-H-5606). A decrease of more than one pencil hardness unit after 7 days immersion at room temperature indicates failure.
- d. Skydrol 500B Fluid Resistance: A decrease of less than two pencil hardness units after 7 days immersion at room temperature is acceptable.
- e. Distilled Water Resistance: A decrease of less than one pencil hardness unit after 4 days immersion at 100°F (37.8°C) is acceptable.

5. Salt Spray Resistance

Test panels, 3 X 8 X 0.02 in (76 X 203 X 0.5 mm) 2024 T3 Alclad aluminum, chromate pretreated and primed with MIL-P-23377, were exposed to 5% salt spray for 500 hours according to ASTM B-117. The test panels were then evaluated for corrosion or loss of adhesion.

6. Humidity Resistance

Test panels, 3 X 8 X 0.02 in (76 X 203 X 0.5 mm) 2024 T3 Alclad aluminum, chromate pretreated and primed with MIL-P-23377, were exposed to 100% relative humidity for 720 hours according to ASTM B-117. After exposure, the test panels were evaluated for loss of adhesion, blistering, softening or other evidence of film failure.

7. Accelerated Weathering

Test panels, 3 X 6 X 0.020 in (76 X 152 X 0.20 mm) 2024 TO Alclad aluminum, chromate pretreated and primed with MIL-P-23377, were exposed for 500 hours in an enclosed twin carbon arc accelerated weathering unit operated on a continuous cycle of 102 minutes of light without water and 18 minutes of light with water spray. After exposure, the coating shall meet the impact flexibility requirements and exhibit no evidence of deterioration or failure such as cracking, checking or loss of adhesion.